Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Simultaneous determination of legacy and emerging per- and polyfluoroalkyl substances in fish by QuEChERS coupled with ultrahigh performance liquid chromatography tandem mass spectrometry

Yan Gao, Qinghe Zhang*, Xiaomin Li, Xiuqin Li, and Hongmei Li

Division of Chemical Metrology and Analytical Science, National Institute of Metrology, Beijing 100029, China

*Corresponding author

Prof. Qinghe Zhang

Division of Chemical Metrology and Analytical Science

National Institute of Metrology

Beijing 100029, China

Tel: 8610-6452-4705

E-mail: zhangqh@nim.ac.cn

Sample collection and preparation

A sea bream sample (Pagrosomus major) was collected from the market for method development, validation and matrix effect evaluation. The fresh fish sample was washed by Mili-Q water first and then dried with blotting paper. After the removal of head, skin, viscera and bones, fish muscle tissue samples were cut into small pieces and then homogenized by a meat mincer at 20000 rpm. Marine fish samples were collected from market of coastal regions in Shandong Province, China. 1-6 fishes of same species from the same site were homogenized as 1 fish composite sample, and 40 fish composite samples were finally prepared. The detailed information of marine fish samples was listed in Table S1.

Quality assurance and quality control

To control background contamination, no fluoropolymer materials were used during sample collection and sample preparation. Equipments for sample collection and sample preparation were rinsed by methanol before use. Solvents and other materials were tested before use.

The method detection limit (MDL) was defined as the concentration exhibiting a signal-to-noise ratio (S/N) of 3 in fish samples and the method quantitation limit (MQL) was determined as the concentration with S/N of 10. Matrix spike recoveries experiment of 3 spiking levels and reference materials (IRMM 427) were used for method validation.

A procedural blank of sample pretreatment was conducted for every 7 samples. For procedure blank, 2 g of mili-q water was used instead of fish samples. The

pretreatment procedures were same with the fish samples. One solution blank of methanol was tested for every 10 injections. PFHpA and 6:2 FTS were detected in the pretreatment and methanol blanks with S/N < 3.

Table S1. Detailed information of marine fish samples

Common name	Scientific Name	Number of fish
Yellow croaker	Larimichthys	1
Yellow croaker	Larimichthys	2
Yellow croaker	Larimichthys	3
Yellow croaker	Larimichthys	4
Yellow croaker	Larimichthys	5
Yellow croaker	Larimichthys	5
Eelpout	Zoarces elongatus	2
Eelpout	Zoarces elongatus	2
Eelpout	Zoarces elongatus	5
Eelpout	Zoarces elongatus	5
Black seabream	Sparus macrocephlus	1
Black seabream	Sparus macrocephlus	1
Black seabream	Sparus macrocephlus	3
Halibut	Hippoglossus stenolepis	1
Halibut	Hippoglossus stenolepis	2
Halibut	Hippoglossus stenolepis	3
Mullet	Sphyraenus	2
Mullet	Sphyraenus	4
Japanese Spanish mackerel	Scomberomorus niphonius	2
Japanese Spanish mackerel	Scomberomorus niphonius	3
Tongue sole	Cynoglossus semilaevis	4
Tongue sole	Cynoglossus semilaevis	4
Japanese halfbeak	Hyporhamphus sajori	3
Japanese halfbeak	Hyporhamphus sajori	6
Silvery pomfret	Pampus argenteus	3
Silvery pomfret	Pampus argenteus	4
Snakeheaded Fish	Channa argus	3
Snakeheaded Fish	Channa argus	3
Flatfish	Cleisthenes herzensteini	5
Monkfish	Lophius litulon	1
Ribbonfish	Coilia ectenes Jordan	3
Ray	Platyrhina sinensis	1
Plaice	Cleisthenes herzensteini	2
Puffer fishes	Tetraodontidae	3
Smelt	Osmerus mordax	1
Pompano	Trachinotus ovatus	2
Japanese sea perch	Lateolabrax japonicus	1
Turbot	Scophthalmus maximus	1
Greenfin horse-faced filefish	Thamnaconus septentrionalis	4
Common hairfin anchovy	Setipinna tenuifilis	4

Table S2. Linearity ranges, calibration curves and regression coefficients (R^2) of target PFASs

Compounds	Calibration curve	Linearity range	R^2
PFBA	y = 34.352x - 3.0050	0.20 - 20 ng/g	0.9985
PFPeA	y = 0.5649x + 0.4160	0.01 - 20 ng/g	0.9987
PFHxA	y = 0.6671x +0.0230	0.02 - 20 ng/g	0.9991
PFHpA	y = 0.9706x - 0.0308	0.01 - 20 ng/g	0.9990
PFOA	y = 1.0199x + 0.0099	0.01 - 20 ng/g	0.9997
PFNA	y = 0.9755x + 0.0221	0.01 - 20 ng/g	0.9993
PFDA	y = 0.9259x + 0.0362	0.01 - 20 ng/g	0.9984
PFUnDA	y = 0.9639x + 0.0086	0.01 - 20 ng/g	1.0000
PFDoDA	y = 0.9637x + 0.0281	0.01 - 20 ng/g	0.9990
PFTrDA	y = 0.6154x + 0.0229	0.01 - 20 ng/g	0.9980
PFTeDA	y = 0.8467x + 0.027	0.01 - 20 ng/g	0.9996
PFHxDA	y = 0.9622x + 0.0243	0.01 - 20 ng/g	0.9997
PFOcDA	y = 0.6760x + 0.0121	0.01 - 20 ng/g	0.9999
PFBS	y = 0.851x + 0.0362	0.01 - 20 ng/g	0.9985
PFPeS	y = 2.5532x + 0.101	0.01 - 20 ng/g	0.9993
PFHxS	y = 1.0372x + 0.0529	0.01 - 20 ng/g	0.9958
PFHpS	y = 0.7463x + 0.0226	0.01 - 20 ng/g	0.9989
PFOS	y = 1.0083x +0.0678	0.01 - 20 ng/g	0.9985
PFNS	y = 0.9685x + 0.0425	0.01 - 20 ng/g	0.9991
PFDS	y = 0.9696x + 0.0584	0.01 - 20 ng/g	0.9983
PFDoS	y = 0.0819x + 0.0046	0.02 - 20 ng/g	0.9979
FOSA	y = 1.3163x +0.0107	0.01 - 20 ng/g	0.9994
N-MeFOSAA	y = 1.1579x + 0.0041	0.01 - 20 ng/g	0.9999
N-EtFOSAA	y = 1.0974x - 0.0164	0.01 - 20 ng/g	0.9993
4:2FTS	y = 0.8587x + 0.0109	0.05 - 5 ng/g	0.9992
6:2FTS	y = 0.9360x + 0.1198	0.01 - 5 ng/g	0.9915
8:2FTS	y = 0.9671x + 0.0164	0.01 - 5 ng/g	0.9992
10:2FTS	y = 0.4102x + 0.0051	0.02 - 5 ng/g	0.9987
6:2Cl-PFAES	y = 1.4922x + 0.0860	0.01 - 20 ng/g	0.9973
8:2Cl-PFAES	y = 0.6609x + 0.0288	0.01 - 20 ng/g	0.9988

Table S3. Comparison of MDLs/MQLs and recoveries with previous studies

Target PFASs	Cleanup method	MDLs	MQLs	Recoveries	Ref
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA,PFHxDA, PFOcDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS, PFOSA, N-MeFOSAA, N-EtFOSAA, 4:2FTS, 6:2FTS, 8:2FTS, 10:2FTS, 6:2ClPFAES, 8:2ClPFAES	QuEChERS	2 -60 pg/g	5-200 pg/g	84.6%-107%	This study
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFOSA, N-MeFOSAA, N-EtFOSAA	WAX	2-120 pg/g	5-300 pg/g	76.6%-109%	27
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFHxPA, PFOPA, PFDPA, PFOSA, N-MeFOSA, N-EtFOSA, N-MeFOSE, N-EtFOSE	QuEChERS		2-13 pg/g	88%-107%	30
PFOA, PFNA, PFOS	QuEChERS	0.16-0.38 ng/g	0.48-1.14 ng/g	70%-133%	32

PFBS, PFHxS, PFOS, PFOPA, PFHxPA, PFDPA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFOSA	WAX	0.2-12.5 ng/g		29%-117%	33
PFOA, PFOS	WAX	0.20-0.47 ng/g	0.50-0.70 ng/g	96%-108%	34
PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS	WAX coupled with Envi-carb		0.02 ng/g	68%-113%	35

Table S4. Results of reference material IRMM 427 (ng/g ww)

Compound	Certified /indicative value	Measured value	SD
PFOS	17 ±4[a]	19.6	0.33
PFDA	1.28 ±0.17[b]	1.38	0.09
PFUnDA	0.74 ±0.20[b]	0.79	0.04
PFDoDA	0.97 ±0.21[b]	1.00	0.02
FOSA	1.60 ±0.50[a]	1.58	0.05
PFNA	0.09 ±0.05[a]	0.09	0.01
PFTrDA	0.62 ±0.29[a]	0.78	0.01
PFTeDA	0.45 ±0.30[a]	0.60	0.03
PFHxS	0.09 ±0.05[a]	0.08	0.01

[a] indicative value

[b] certified value

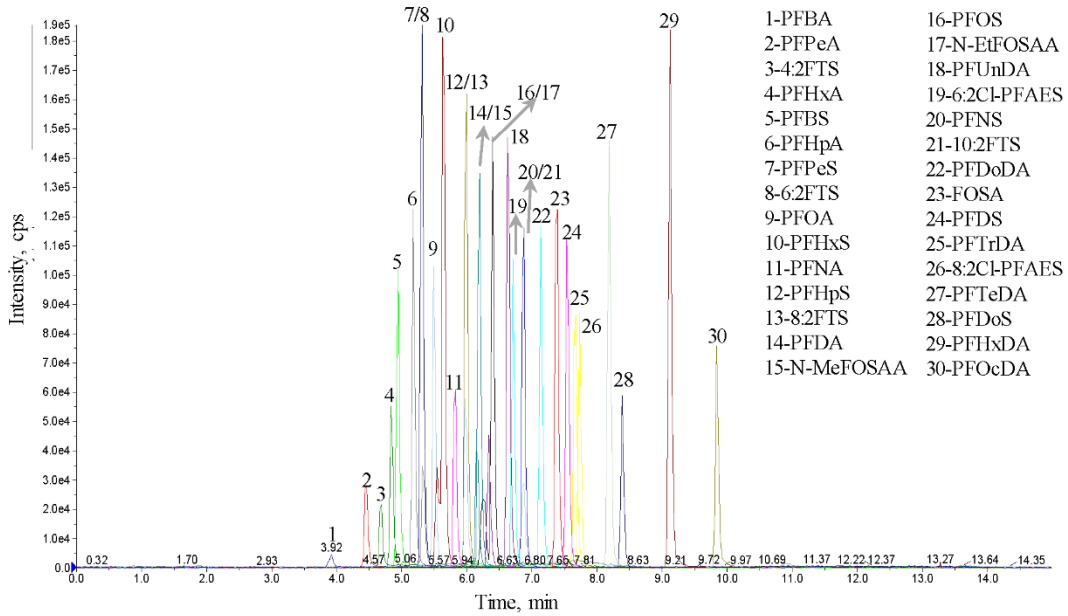
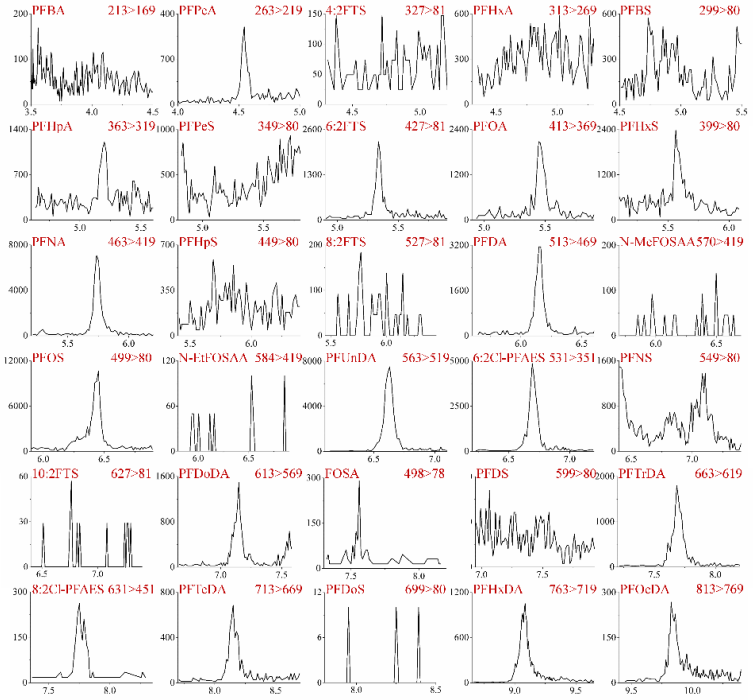
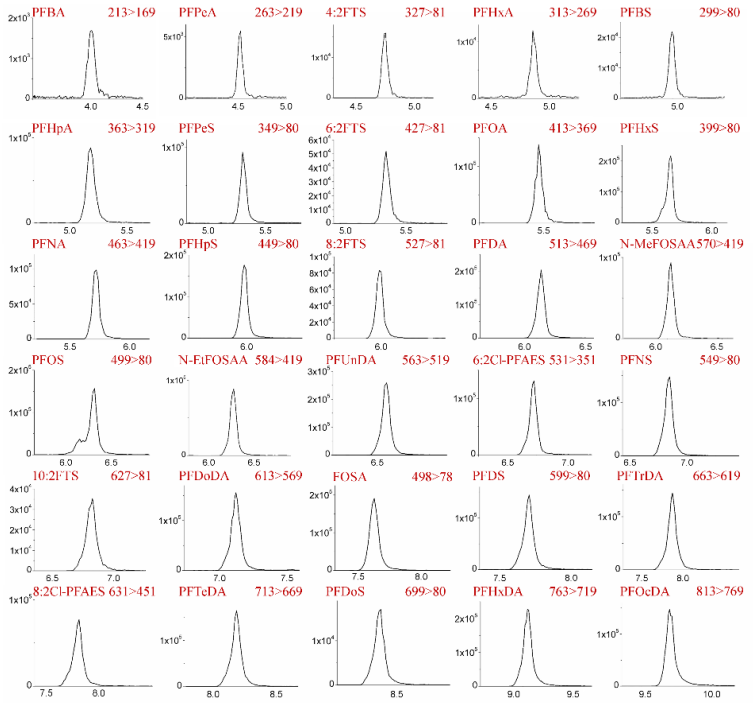


Figure S1. Chromatograms of UHPLC-MS/MS analysis of 30 target PFASs



a



b

Figure S2. Chromatograms of real fish sample (a) and fortified fish sample (b) after QuEChERS procedure

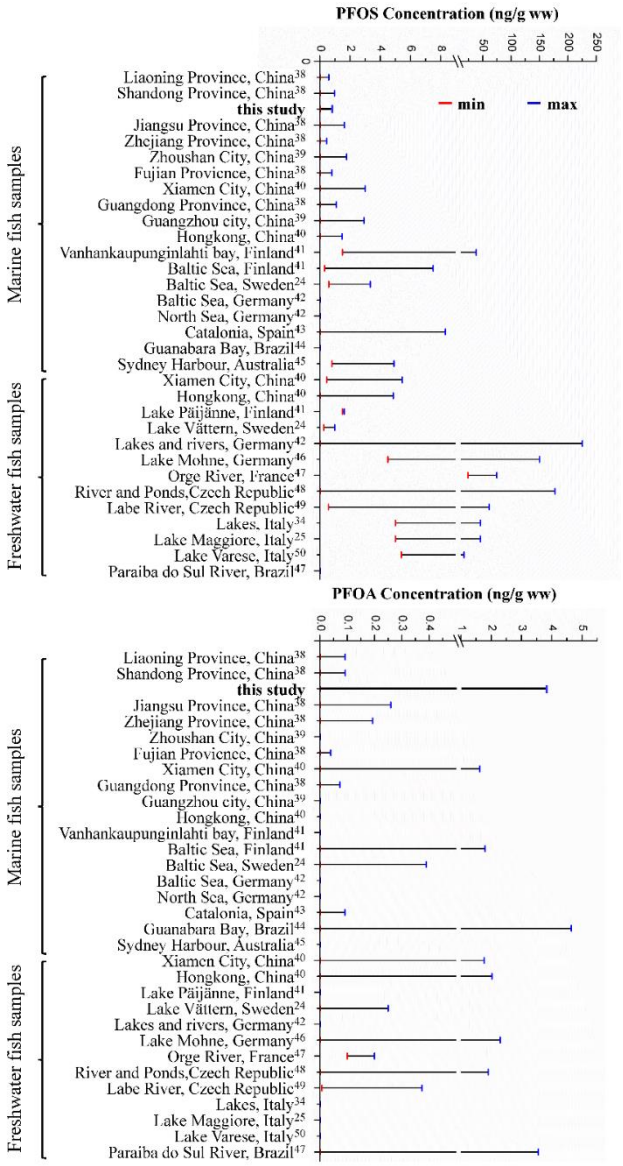


Figure S3. Comparison of PFOS and PFOA concentrations in marine fish samples and freshwater fish samples worldwide