Supporting Information

Enhancing Sensitivity in Miniature Mass Spectrometry Analysis via Dicationic Ionic Liquid-Based Matrix-Assisted Ionization and Charge Inversion Reactions

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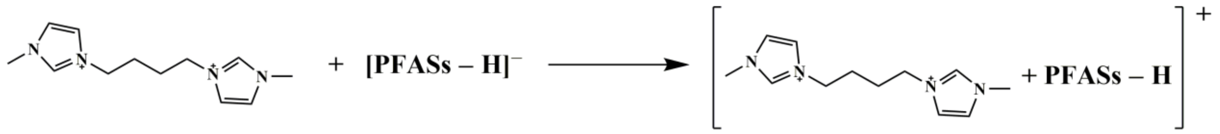
Supplementary Scheme



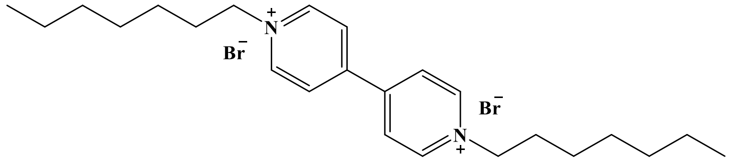
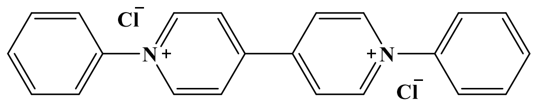
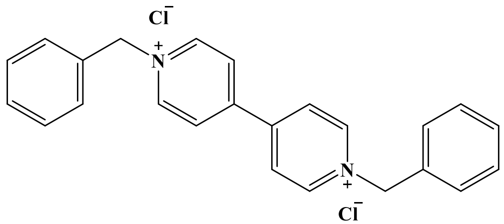
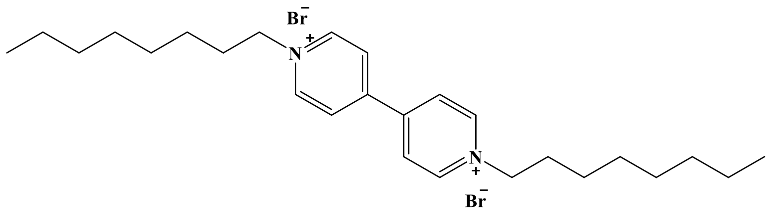
Scheme S1. Complexation of the imidazolium-based dicationic ionic liquid (DIL) with deprotonated per- and polyfluoroalkyl substances (PFAS).

Supplementary Tables

Table S1. Chemical information of four investigated PFAS.

PFAS	Abbreviation	Formula	CAS	MW	LogKow
Perfluorooctanesulfonic acid	PFOS	$C_8HF_{17}O_3S$	1763-23-1	500.13	4.49
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	335-67-1	414.07	4.81
Perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	375-95-1	464.08	5.48
Perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	335-76-2	514.08	6.15

Table S2. Chemical information of eight investigated DIL.

No.	DIL	Structure	Formula	MW
1	1,1'-Diheptyl-4,4'-bipyridinium dibromide		$C_{24}H_{38}Br_2N_2$	512.14
2	1,1'-Diphenyl-4,4'-bipyridinium dichloride		$C_{22}H_{18}Cl_2N_2$	380.08
3	1,1'-Dibenzyl-4,4'-bipyridinium dichloride		$C_{24}H_{22}Cl_2N_2$	408.12
4	1,1'-Dioctyl-4,4'-bipyridinium dibromide		$C_{26}H_{42}Br_2N_2$	540.17

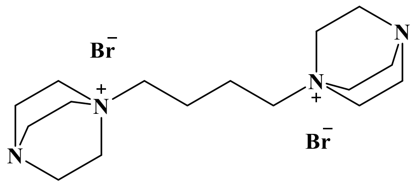
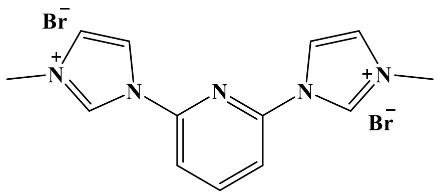
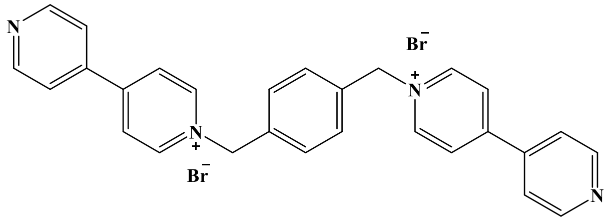
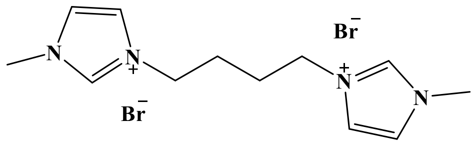
5	1,1'-(Butane-1,4-diyl)bis[4-aza-1-azoniabicyclo[2.2.2]octane] dibromide		$C_{16}H_{32}Br_2N_4$	438.09
6	1,1'-(2,6-Pyridinediyl)bis(3-methylimidazolium) dibromide		$C_{13}H_{15}Br_2N_5$	398.97
7	1,1'-[1,4-Phenylenebis(methylene)]bis(4,4'-bipyridinium) dibromide		$C_{28}H_{24}Br_2N_4$	574.04
8	1,1-Bis(3-methylimidazolium-1-yl) butylene dibromide		$C_{10}H_{20}Br_2N_4$	380.12

Table S3. Instrument parameters for the analysis of four PFAS using a miniature mass spectrometer.

PFAS	Injection size (ms)	CID AC amplitude (V)	Precursor ion (*m/z*)	Product ion 1 (*m/z*)	Product ion 2 (*m/z*)
PFOS	39	1.56	719.1	636.8	219.1
PFOA	39	1.75	633.1	219.1	138.1
PFNA	41	1.98	683.1	219.1	
PFDA	40	2.23	733.1	219.1	

Table S4. Comparison of the developed method with other approaches reported in the literature for the analysis of PFAS in water samples.

No.	Sample	Analyte	Method	LOD	LOQ	Recovery/%	RSD/%	Time	Reference
1	Environmental water, tap water, and swimming pool water	4 PFAS	MAI-Mini MS	5 μg/L	10 μg/L	86.6–106.3	3.5–7.2	< 1 min	This work
2	Lake water	11 PFAS	SPE-UHPLC-MS/MS	0.03–1.9 ng/L	0.09–5.8 ng/L	97.3–113.0	1.0–9.0	> 5 min	1
3	Superficial and underground water	12 PFAS	SPE-HPLC-MS/MS	/	0.2–5 ng/L	81.0–107.2	8.3–13.8	> 10 min	2
4	Estuarine water	23 PFAS	SPE-UHPLC-MS/MS	0.48–1.68 pg/5μL	1.71–5.40 pg/5μL	78.54–112.61	/	> 8 min	3
5	Tap water, river water, and waste water	4 PFAS	SPE-UHPLC-MS/MS	0.04–0.05 ng/L	0.15–0.20 ng/L	94.5–101.5	1.1–8.3	> 30 min	4
6	Reservoir water	12 PFAS	UHPLC-MS/MS	0.02–0.48ng/L	0.08–1.58ng/L	51.1–122.3	0.1–17.5	> 30 min	5
7	Textiles and food packaging materials	10 PFAS	UHPSFC-MS/MS	0.2–1.6 μg/kg	0.6–3.2 μg/kg	71.3–110.7	0.9–8.6	> 30 min	6

Table S5. The F-test and T-test results along with their corresponding p-values for assessing the consistency of results between the developed method and traditional UHPLC-MS/MS method.

Method	Detected concentration (μg/L, *n*=3)	F-test result	Two-tailed T-test result
This work	13.0, 14.2, 13.8	P = 0.9372 > 0.05	P = 0.1557 > 0.05
UHPLC-MS/MS	12.1, 12.8, 13.4	insignificant	insignificant

Table S6. Greenness assessment of the developed method using three well-established metric tools (GAPI, AGREE, and BAGI).

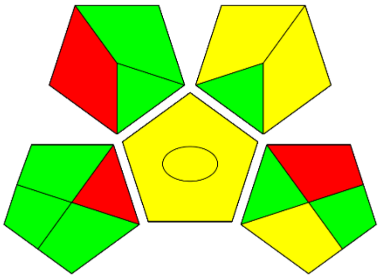
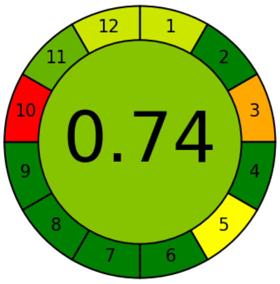
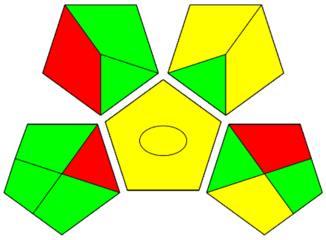
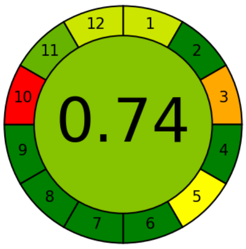
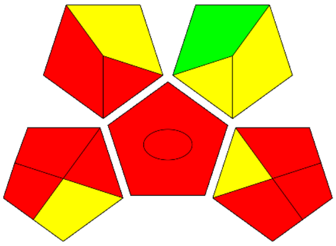
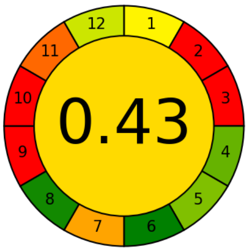
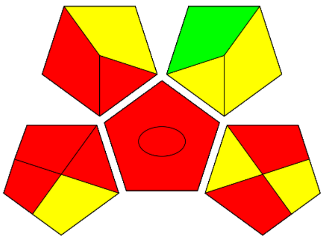
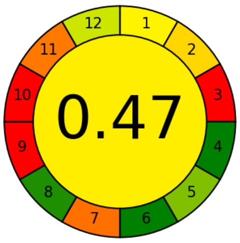
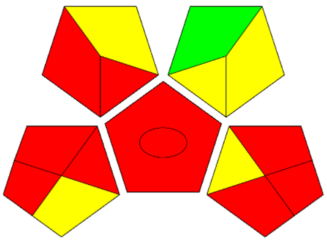
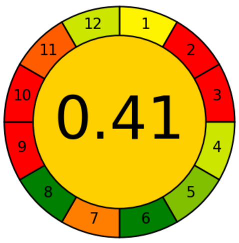
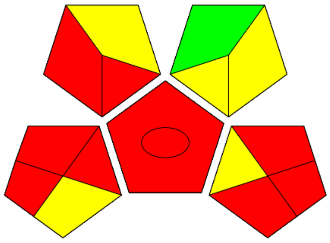
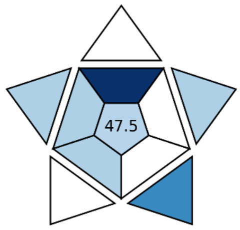
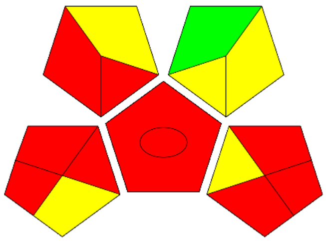
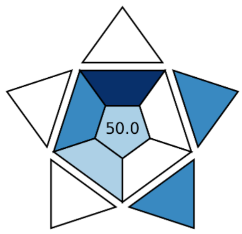
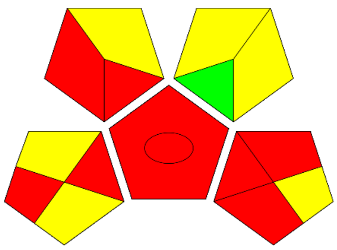
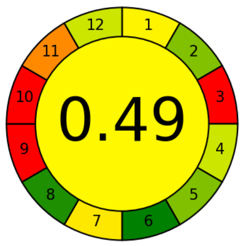
GAPI	**AGREE**	**BAGI**
		
First pentagram P1: Sample collection: Off-line P2: Sample preservation: None P3: Sample transport: None P 4: Sample storage: None Second pentagram P 5: Type of method: Simple procedures Third pentagram P 6: Scale of extraction: Nano-extraction P 7: Solvents/reagents used: No-green solvents/reagents used P 8: additional treatments: None Fourth pentagram P 9: Amount of reagents or solvents: < 10 mL P 10: Health Hazard: Moderately toxic P 11 Safety hazard: Flammability score 2 Fifth pentagram P 12: Energy per sample: < = 0.1 kWh P 13: Occupational hazard: Emission of vapors to the atmosphere P 14: Waste: < 1 mL P 15: Waste treatment: Degradation	P1: At-line P2: 0.001 mL P3: At-line P4: 3 or fewer P5: Manual and none or miniaturized P6: No derivatization P7: 0.001 mL P8: 4 analytes in single run, 60 sample per hour P9: 0.1kWh P10: None of the reagents are bio-based P11: 0.001 mL P12: Toxic to aquatic life and highly flammable	P1: Quantitative and Confirmatory P2: Multi-element analysis for 2–5 compounds of the same chemical class P3: Simple in operation portable instrumentation P4: 2–12 P5: Simple sample preparation required P6: > 10 P7: Commercially available reagents that are noncommon in QC labs P8: No preconcentration is required P9: Manual treatment and analysis P10: < = 10 mL environmental

Table S7. Comparison of greenness assessment results of the developed method and other traditional analytical methods using three well-established metric tools (GAPI, AGREE, and BAGI).

Method	GAPI	AGREE	BAGI	Reference
MAI-Mini MS				**This work**
SPE-UHPLC-MS/MS				**1**
SPE-HPLC-MS/MS				**2**
SPE-UHPLC-MS/MS				**3**

SPE-UHPLC-MS/MS				**4**
UHPLC-MS/MS				**5**
UHPSFC-MS/MS				**6**

Supplementary Figures

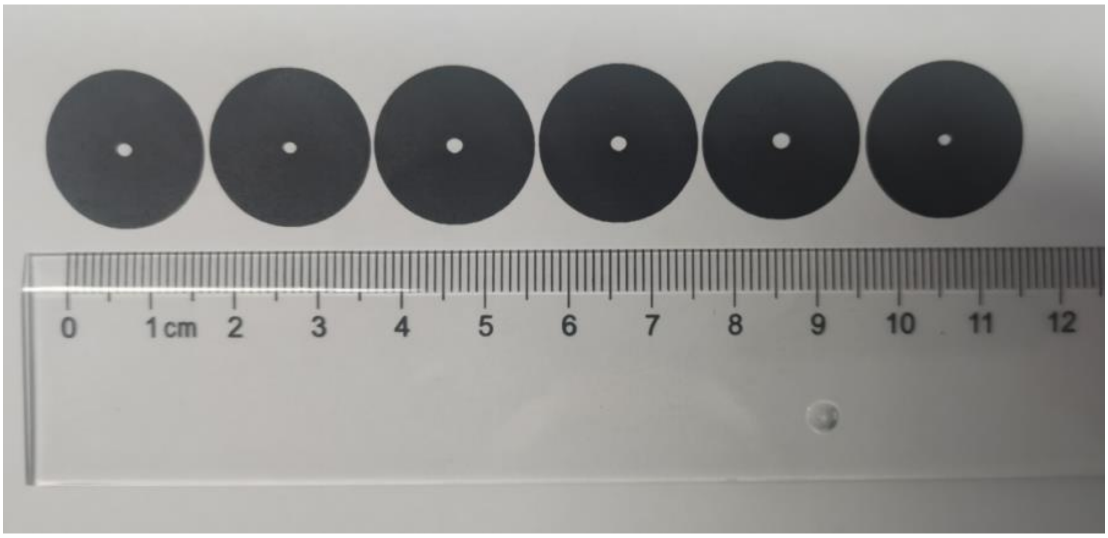


Figure S1. Photo of the wax-printing sample microspot array after pattern fixation.

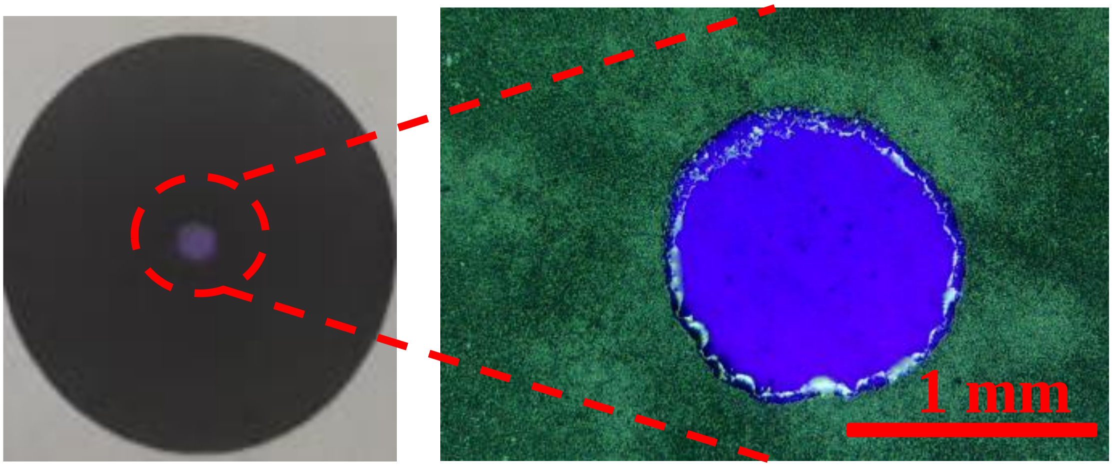


Figure S2. Photo of the Disperse Blue 1 solution confined by the waxed surrounding area.

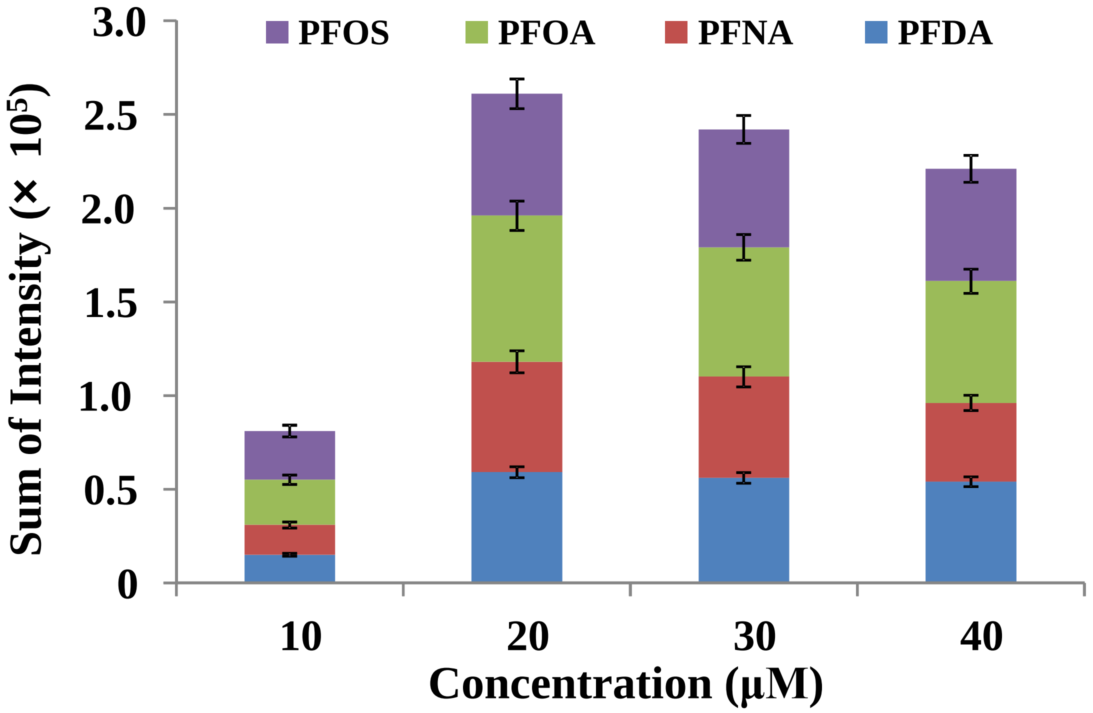


Figure S3. Optimization of the concentration of $C_4(MIM)_2F_2$.

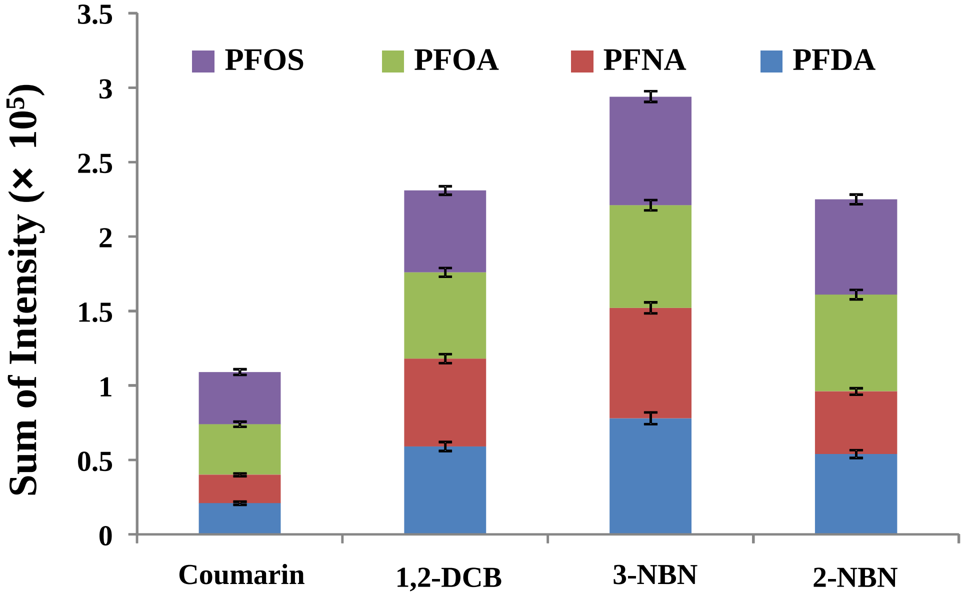


Figure S4. Optimization of four matrix-assisted ionization (MAI) matrices.

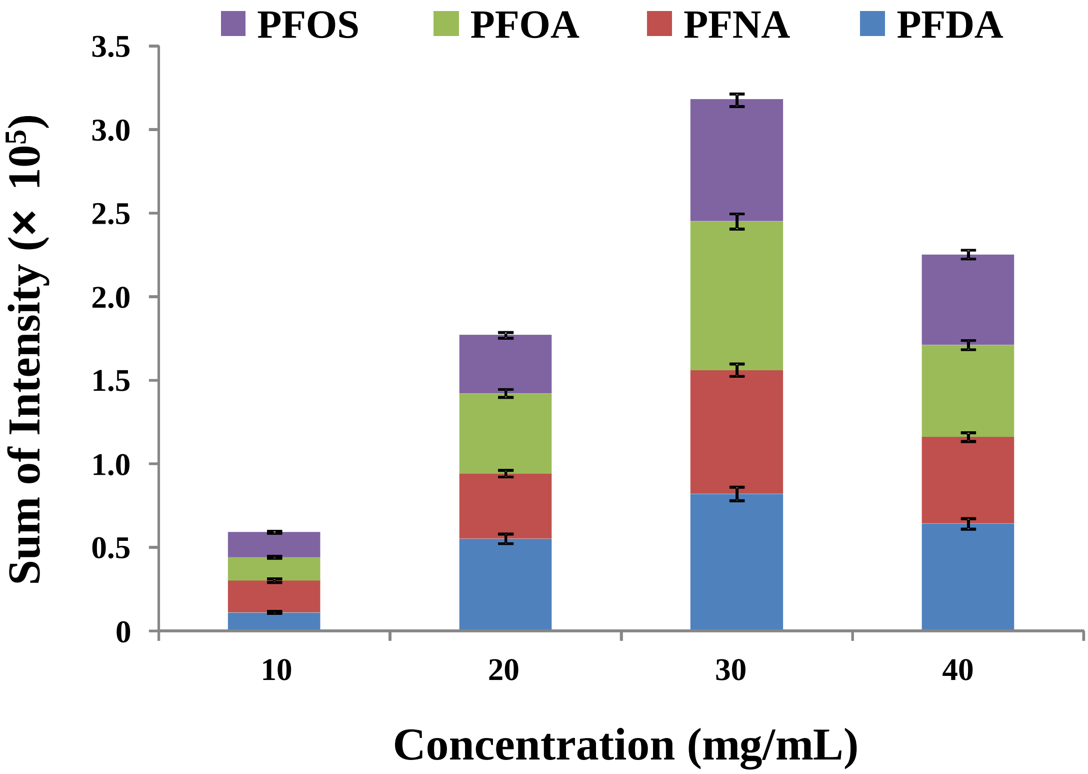


Figure S5. Optimization of the concentration of 3-nitrobenzonitrile (3-NBN).

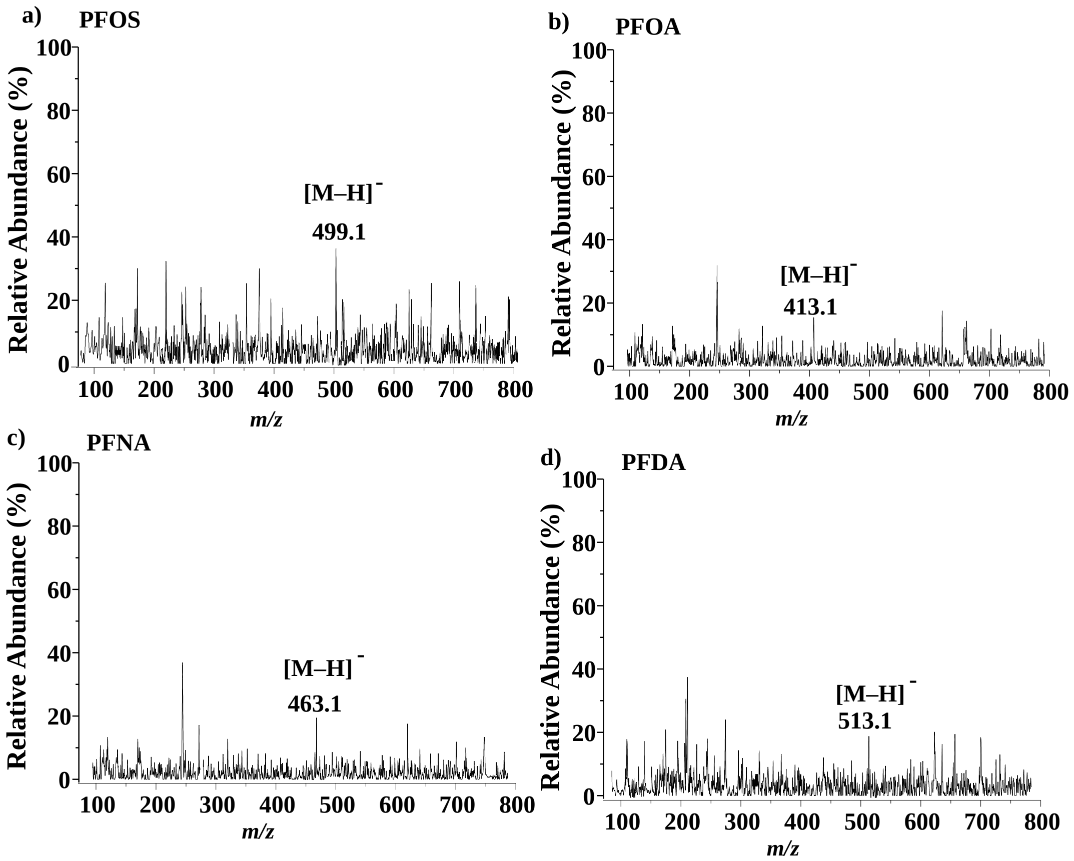


Figure S6. MS spectra of PFOS (a), PFOA (b), PFNA (c), and PFDA (d) in negative mode without DILs.

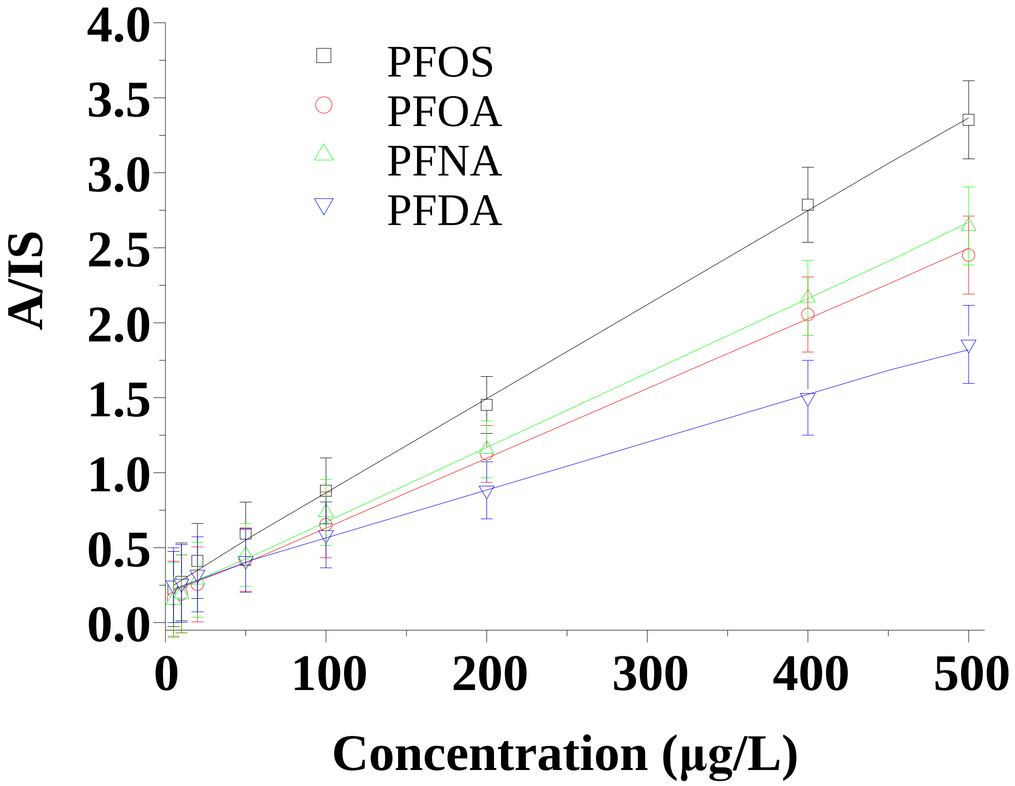


Figure S7. Calibration curves of four investigated PFAS.

Figure S8. Geographical map of the sampling sites. GPS coordinates of the sampling sites are as follow:

1: Longitude 116.314474, Latitude 40.132104

2: Longitude 116.705309, Latitude 40.119746

3: Longitude 116.284614, Latitude 39.990074

4: Longitude 116.633157, Latitude 39.923817

5: Longitude 116.526654, Latitude 39.779353

6: Longitude 116.387956, Latitude 39.982224

7: Longitude 116.192053, Latitude 39.913136

8: Longitude 116.514437, Latitude 39.906274

9: Longitude 116.394567, Latitude 39.861759

10: Longitude 116.517599, Latitude 39.816773

11: Longitude 116.307467, Latitude 39.936597

12: Longitude 116.323278, Latitude 39.880587

13: Longitude 116.550944, Latitude 39.949431

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