NEMC, August 7, 2025

Analysis of Ultrashort-Chain PFAS by Reversed-Phase LC/MS/MS

Yongtao (Bruce) Li

Eurofins Eaton Analytical, LLC

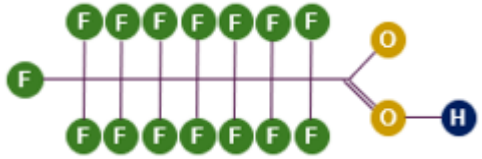
eurofins | Environment Testing

Presentation Outline

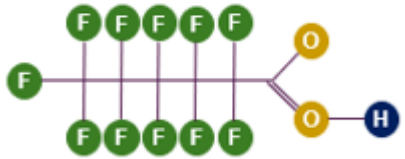
- Introduction
- Method Development and Validation
- Matrix Interferences
- Field Sample Analysis and Results
- Conclusions

Per- and Polyfluoroalkyl Substances (PFAS)

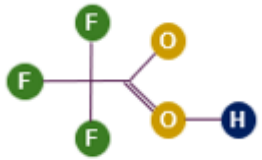
PFOA



PFHxA



TFA



- Long-chain PFAS (C7 and longer) — PFOA, PFOS, PFNA, PFHpA, etc.
- Short-chain PFAS (C4-C6) — PFBS, PFHxS, HFPO-DA or GenX, PFBA, PFPeA, PFHxA, etc.
- Ultrashort-chain PFAS (C1-C3) — TFA, PFPrA, TFMS, etc.

Ultrashort-Chain PFAS of Interest

eurofins | Environment Testing

PFAS	Acronym	CAS #
Trifluoroacetic acid	TFA	76-05-1
Perfluoropropanoic acid	PFPrA	422-64-0
Perfluoromethoxy acetic acid	PFMOAA	674-13-5
Trifluoromethanesulfonic acid	TFMS	1493-13-6
Perfluoroethanesulfonic acid	PFEtS	354-88-1
Perfluoropropanesulfonic acid	PFPrS	423-41-6
Bis(trifluoromethane)sulfonimide	TFSI	82113-65-3
2,3,3,3-Tetrafluoropropanoic acid	2,3,3,3-TFPrA	359-49-9
2,2,3,3-Tetrafluoropropanoic acid	2,2,3,3-TFPrA	756-09-2

Ultrashort-Chain PFAS Applications

eurofins | Environment Testing

PFAS	Applications
TFA	A strong organic acid used in various applications, including as a solvent, catalyst, and in peptide synthesis, a degradation product of refrigerants like HFCs and HFOs .
PFPrA	A surfactant, in polymer synthesis, an intermediate in the production of other fluorinated compounds, and a potential catalyst in certain chemical reactions.
PFMOAA	Used in various consumer products.
TFMS	A strong acidic catalyst in various organic synthesis reactions, a solvent, used in the synthesis of pharmaceuticals, polymers, and specialty chemicals.
PFEtS	A surfactant and protective coating substance, a superacid in chemical reactions and in the synthesis of ion-exchange membranes.
PFPrS	Manufacturing of aqueous film forming foam (AFFF).
TFSI	Electrolytes for lithium-ion batteries and in organic synthesis.

Ultrashort-Chain PFAS Toxicity

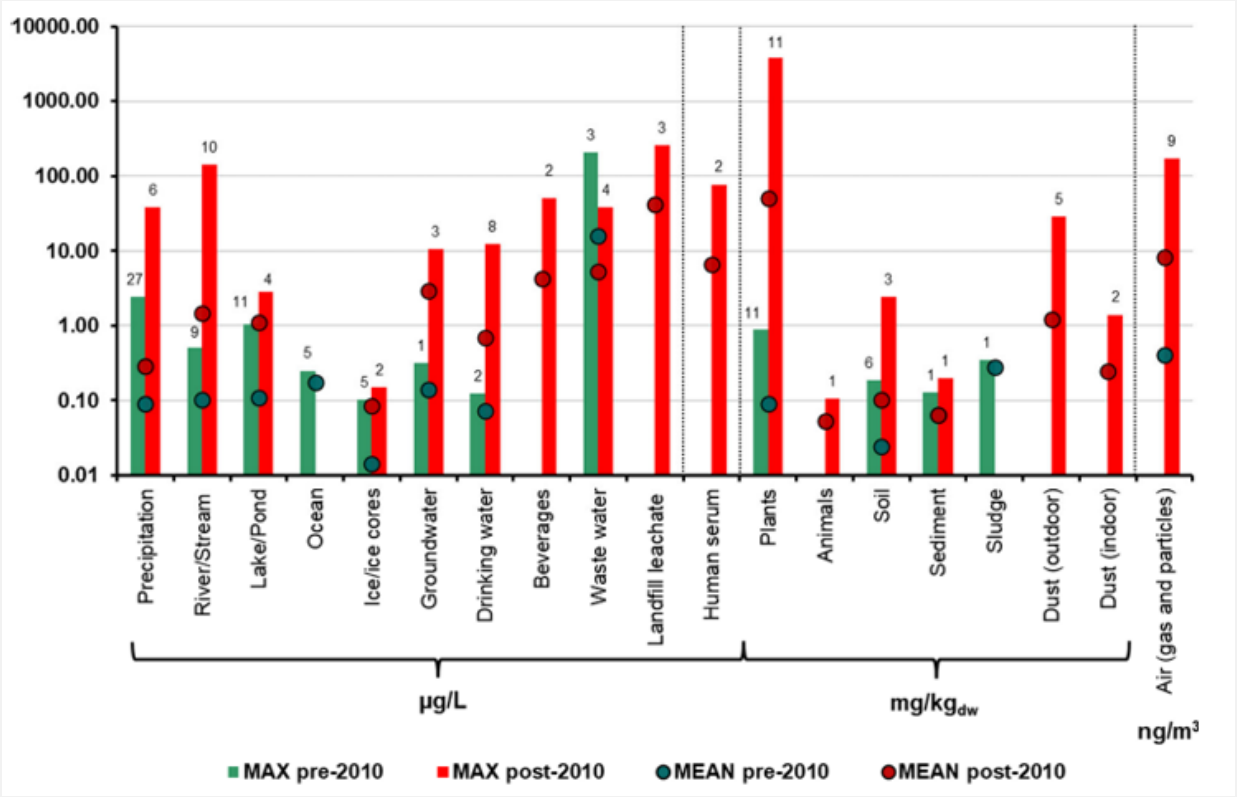
- TFA is not considered carcinogenic or a reproductive/developmental toxicant in humans. Mammalian toxicity studies suggest that TFA may have potential reproductive and liver toxicity.
- The U.S. EPA has established a chronic reference dose (RfD) of 0.0001 mg/kg per day for PFPrA, suggesting a level of exposure considered safe for a lifetime.
- PFMOAA is considered a maternal and developmental toxicant.
- There is growing evidence of the toxicity of some ultrashort-chain PFAS, however, their effects on human health and ecosystems remain largely unknown.

Ultrashort-Chain PFAS Occurrence

- Ultrashort-chain PFAS are extremely persistent and mobile in the environment.
- They are widely present in the environment, human bodies, and potable water as well.
- Pesticide Action Network Europe (PAN Europe) reported that TFA was detected in 94% of the drinking water samples at concentrations of up to 4,100 ng/L with an average of 740 ng/L, and in 63% of the bottled water samples at concentrations of up to 3,200 ng/L with an average of 278 ng/L.

Ultrashort-Chain PFAS Occurrence (Cont'd)

- Arp et al, the global threat from the irreversible accumulation of trifluoroacetic acid (TFA), *Environ. Sci. Technol.* 2024, 58, 19925−19935.



Ultrashort-Chain PFAS Regulations

- Currently, there are no specific regulations or maximum contaminant levels (MCLs) established for the ultrashort-chain PFAS.
- The new EU Drinking Water Directive of 500 ng/L for total PFAS will be implemented in 2026. It is not clear if TFA is excluded.
- European regulations are discussing harmonized classification and labeling of TFA as a relevant metabolite under the Drinking Water Directive with a limit of 100 ng/L in drinking water.
- The Dutch National Institute for Public Health and the Environment (RIVM) proposed drinking water guideline for TFA of 2,200 ng/L.
- Some ultrashort-chain PFAS may be potential UCMR6 candidates.

Suitable Analytical Techniques for Ultrashort-Chain PFAS

- Ion chromatography/tandem mass spectrometry (IC/MS/MS)
- Liquid chromatography/tandem mass spectrometry (LC/MS/MS)
  - Reversed-phase Liquid chromatography (RPLC)
  - Hydrophilic interaction liquid chromatography (HILIC)
  - Hybrid HILIC/ion exchange (IX) columns

Method Development & Validation

- Collect water samples in PP bottles.
  - No sample preservation.
  - Collect field reagent blanks.
- Store samples at or below 6 °C for up to 14 days.
- Add ascorbic acid and internal standards.
- Store prepared samples at room temperature for up to 28 days.
- C18/positive surface mixed-mode column.

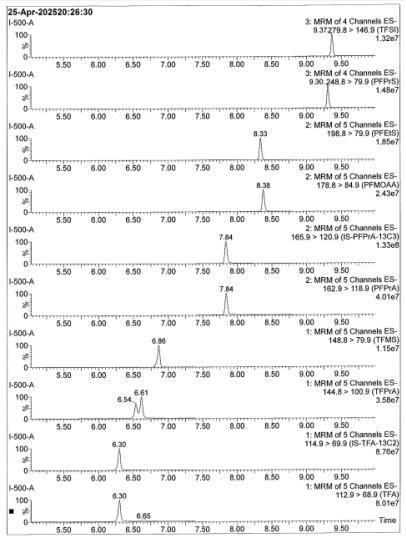
DAI–LC/MS/MS Process

25 – 100 mL

10 mL

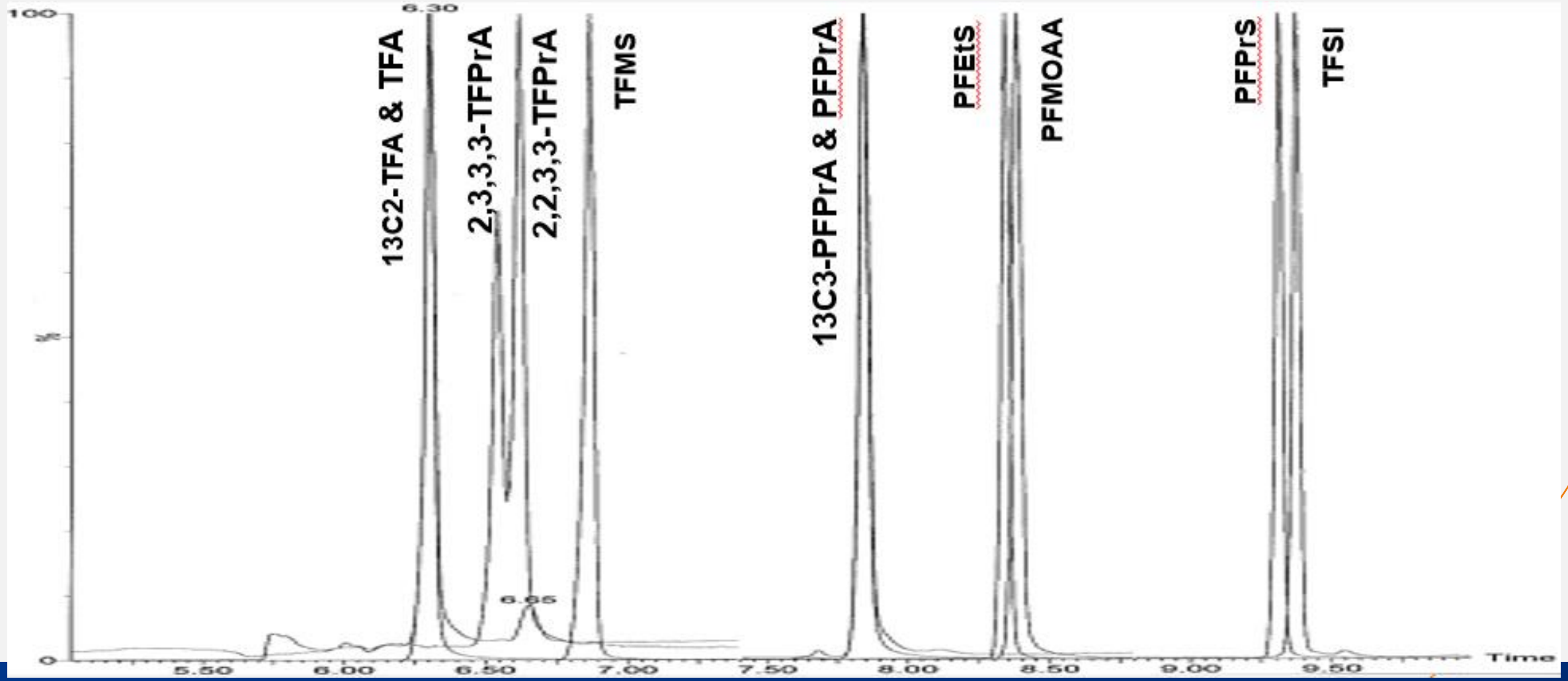
0.3 – 2 mL

IS + Ascorbic Acid

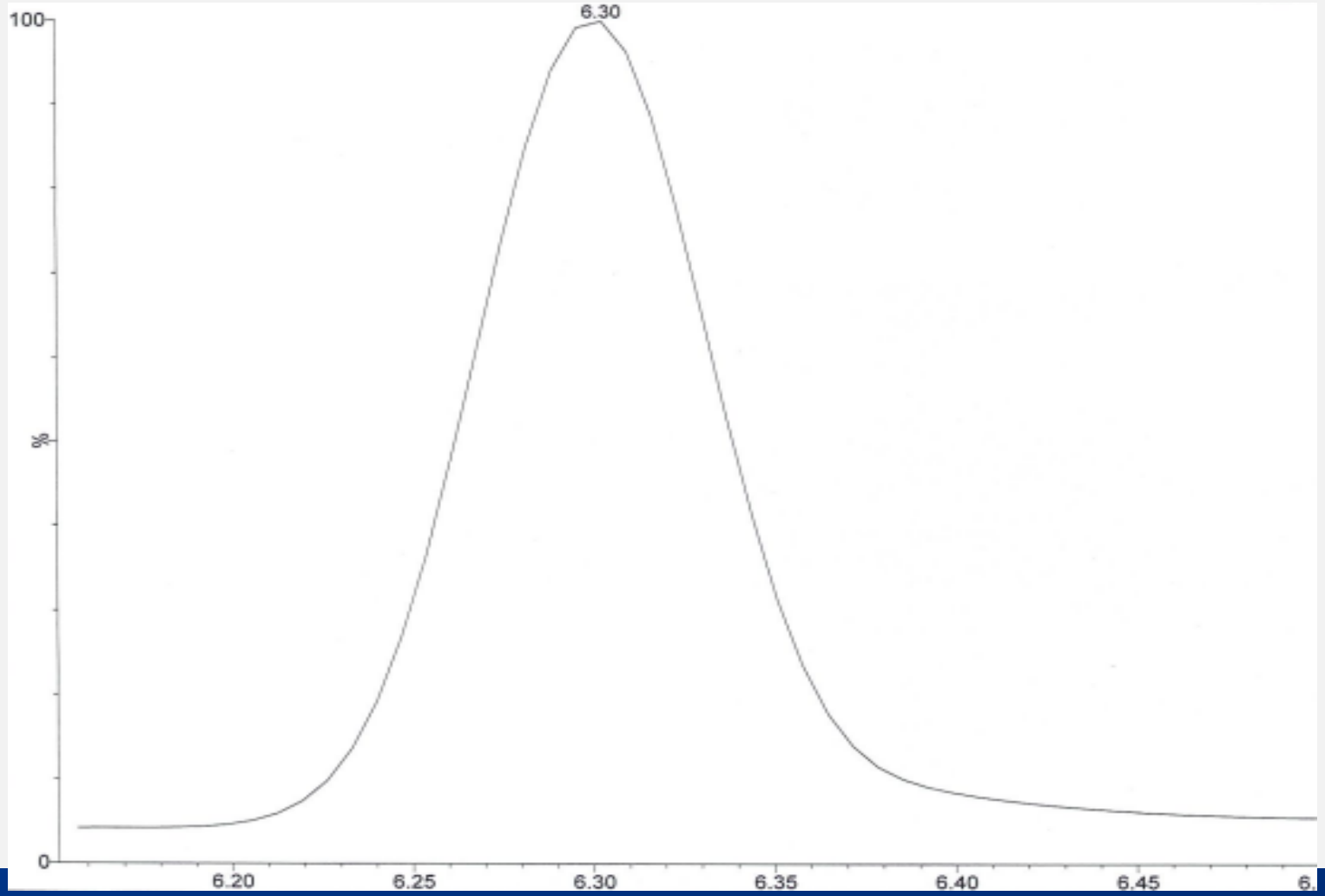


eurofins | Environment Testing

Chromatograms



TFA Peak Asymmetry Factor = 0.9



eurofins | Environment Testing

IDC – Sensitivity

PFAS	LCMRL (ng/L)	DL (ng/L)	MDL (ng/L)	MRL (ng/L)	Upper PIR (%)	Lower PIR (%)
TFA	19	9.6	2.5	20	93	86
PFPrA	3.7	2.1	0.97	5	99	92
PFMOAA	0.40	0.18	0.31	1	108	103
TFMS	0.51	0.26	0.18	1	144	136
PFEtS	0.056	0.0032	0.20	0.1	119	107
PFPrS	0.028	0.011	0.14	0.1	123	115
TFSI	0.038	0.0049	0.25	0.1	115	106
2,3,3,3-TFPrA	1.8	0.82	1.4	5	104	96
2,2,3,3-TFPrA	2.9	0.80	0.61	5	110	101

PIR = Prediction Interval of Results

IDC – Accuracy & Precision (Initial Test)

eurofins | Environment Testing

PFAS	Target (ng/L)	Ave. Rec. (%) n = 7	RSD (%) n = 7
TFA	500	106	2.6
PFPrA	200	103	2.6
PFMOAA	500	114	2.2
TFMS	50	100	2.8
PFEtS	50	98	2.7
PFPrS	50	97	2.6
TFSI	25	103	2.6
2,3,3,3-TFPrA	500	97	4.0
2,2,3,3-TFPrA	500	105	2.9

IDC – Accuracy & Precision (Mid-Levels)

eurofins | Environment Testing

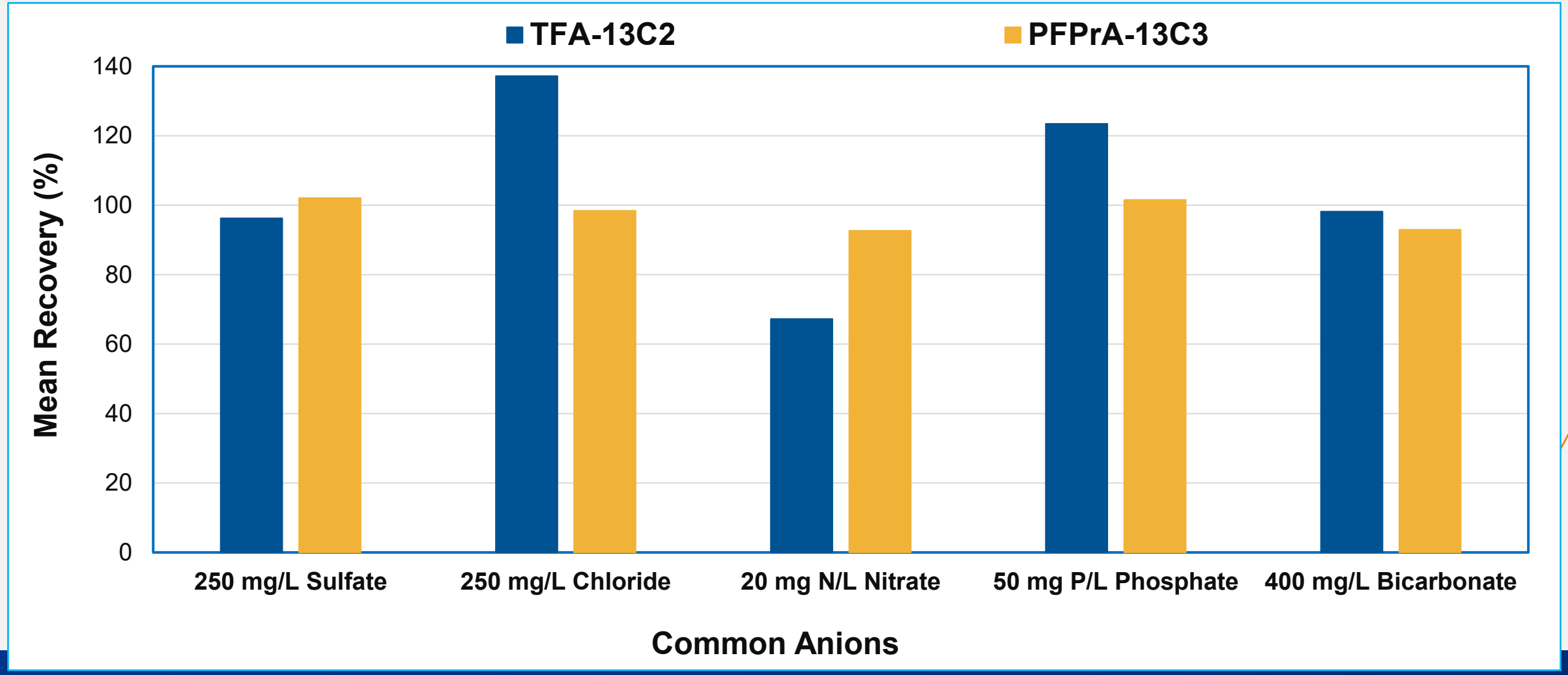
PFAS	Target (ng/L)	Ave. Rec. (%) n = 7	RSD (%) n = 7
TFA	400	106	1.1
PFPrA	100	105	1.0
PFMOAA	20	102	1.8
TFMS	20	92	1.4
PFEtS	2	105	1.2
PFPrS	2	105	1.5
TFSI	25	104	1.4
2,3,3,3-TFPrA	100	90	1.3
2,2,3,3-TFPrA	100	97	2.6

IDC – Accuracy & Precision (MRLs)

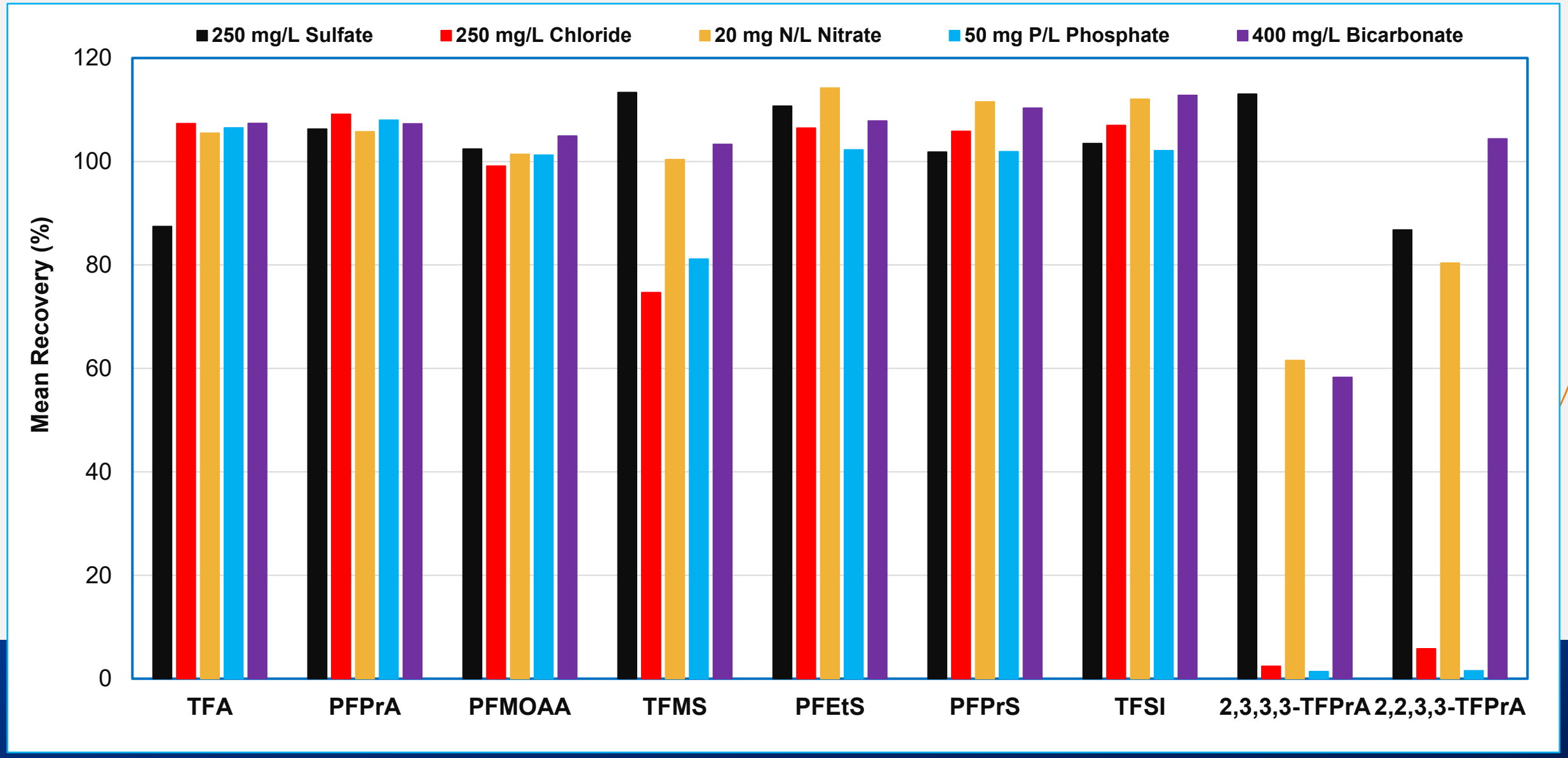
eurofins | Environment Testing

PFAS	Target (ng/L)	Ave. Rec. (%) n = 7	RSD (%) n = 7
TFA	20	89	3.8
PFPrA	5	96	3.8
PFMOAA	1	106	2.6
TFMS	1	140	2.7
PFEtS	0.1	113	5.3
PFPrS	0.1	119	3.7
TFSI	0.1	111	4.1
2,3,3,3-TFPrA	5	100	4.1
2,2,3,3-TFPrA	5	106	3.9

Impacts of Common Anions – IS (n = 4)



Impacts of Common Anions – Analytes (n = 4)

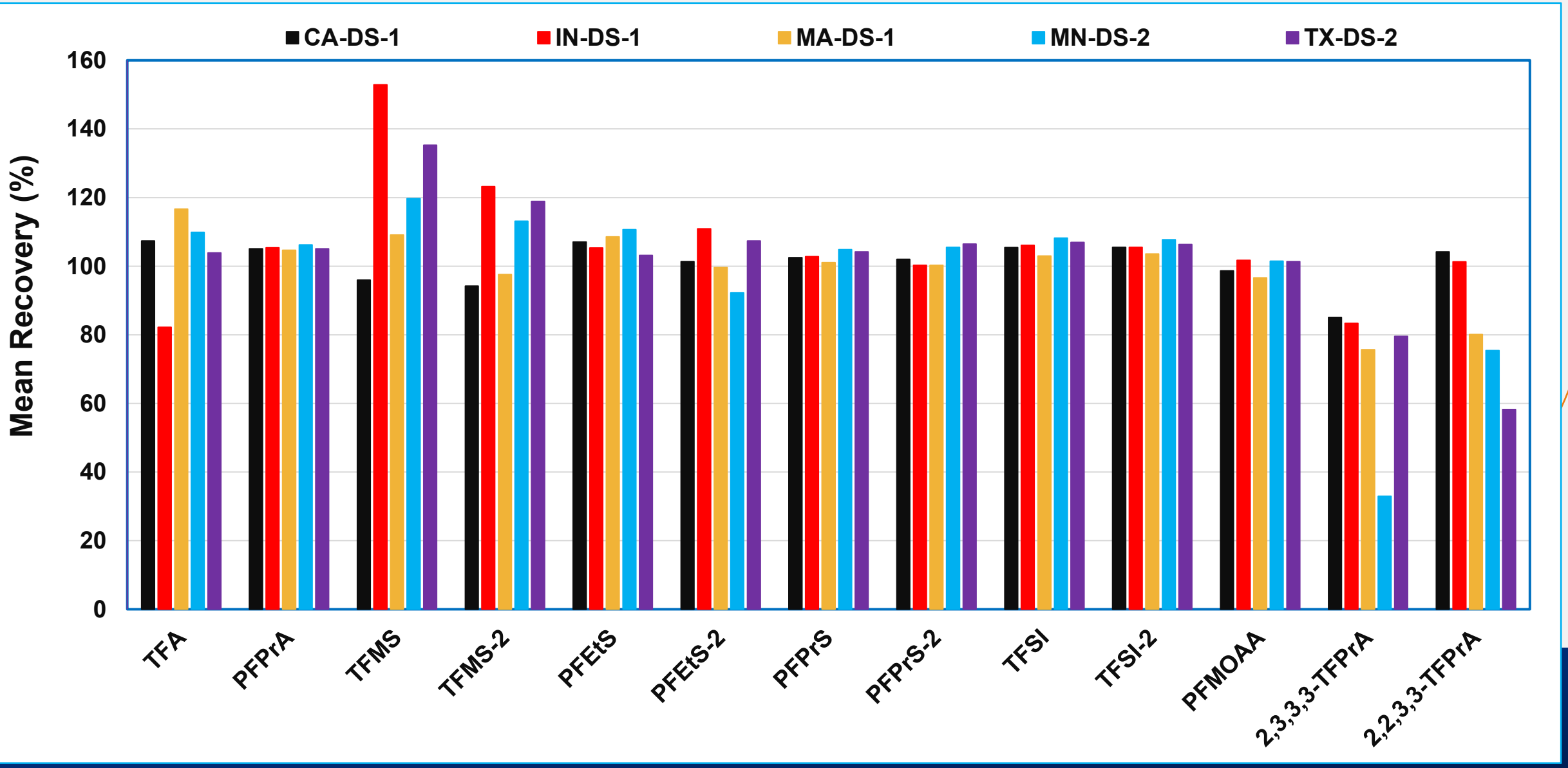


Local Tap Water Matrix Spikes (n =4)

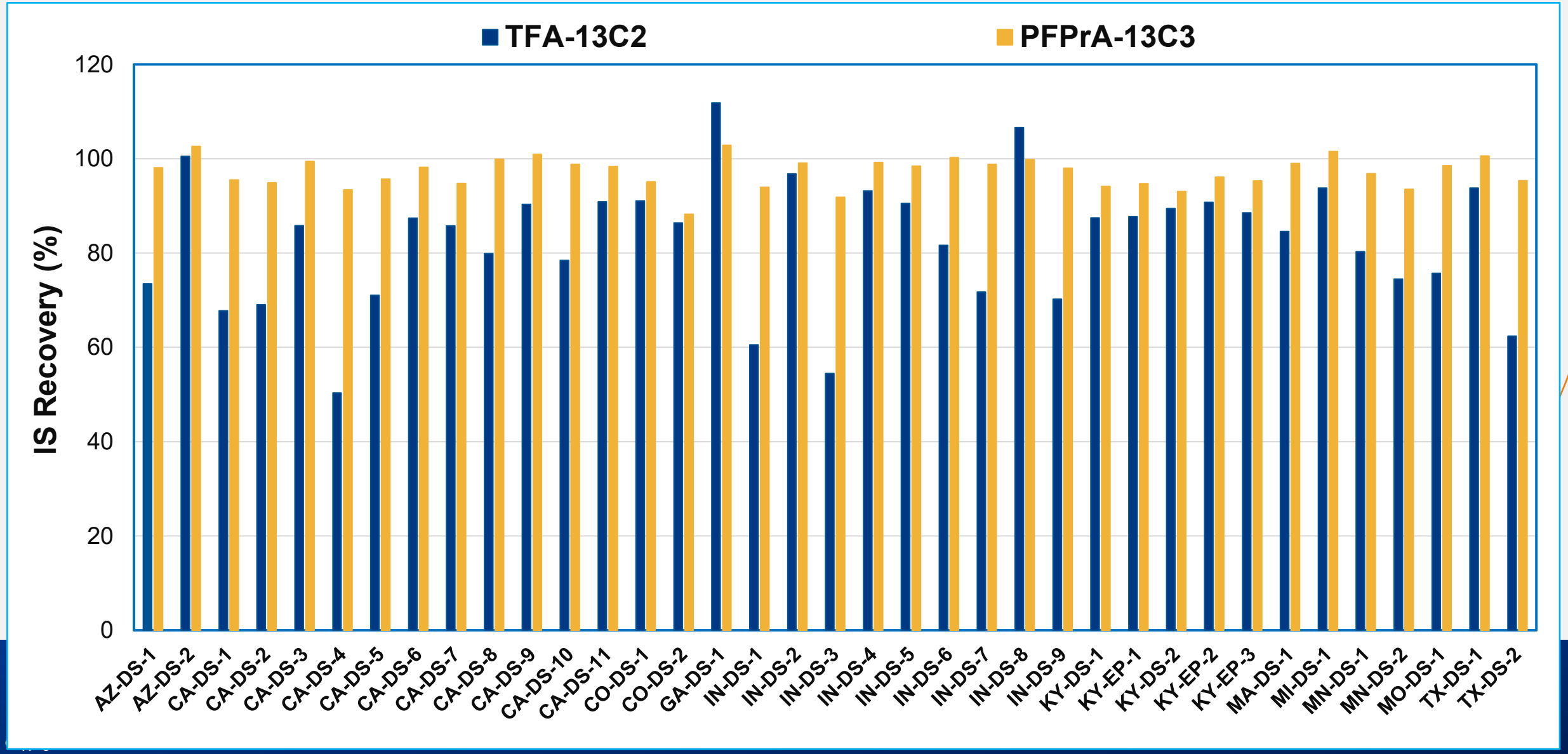
eurofins | Environment Testing

PFAS	Native (ng/L)	Target (ng/L)	Ave. Rec. (%) n = 7	RSD (%) n = 7
TFA	639	500	106	1.0
PFPrA	8.4	200	102	1.9
PFMOAA	<0.1	500	111	1.8
TFMS	5.9	50	140	0.8
PFEtS	0.10	50	100	2.0
PFPrS	0.28	50	98	2.1
TFSI	0.14	25	104	2.0
2,3,3,3-TFPrA	<5.0	500	129	1.9
2,2,3,3-TFPrA	<5.0	500	132	2.0

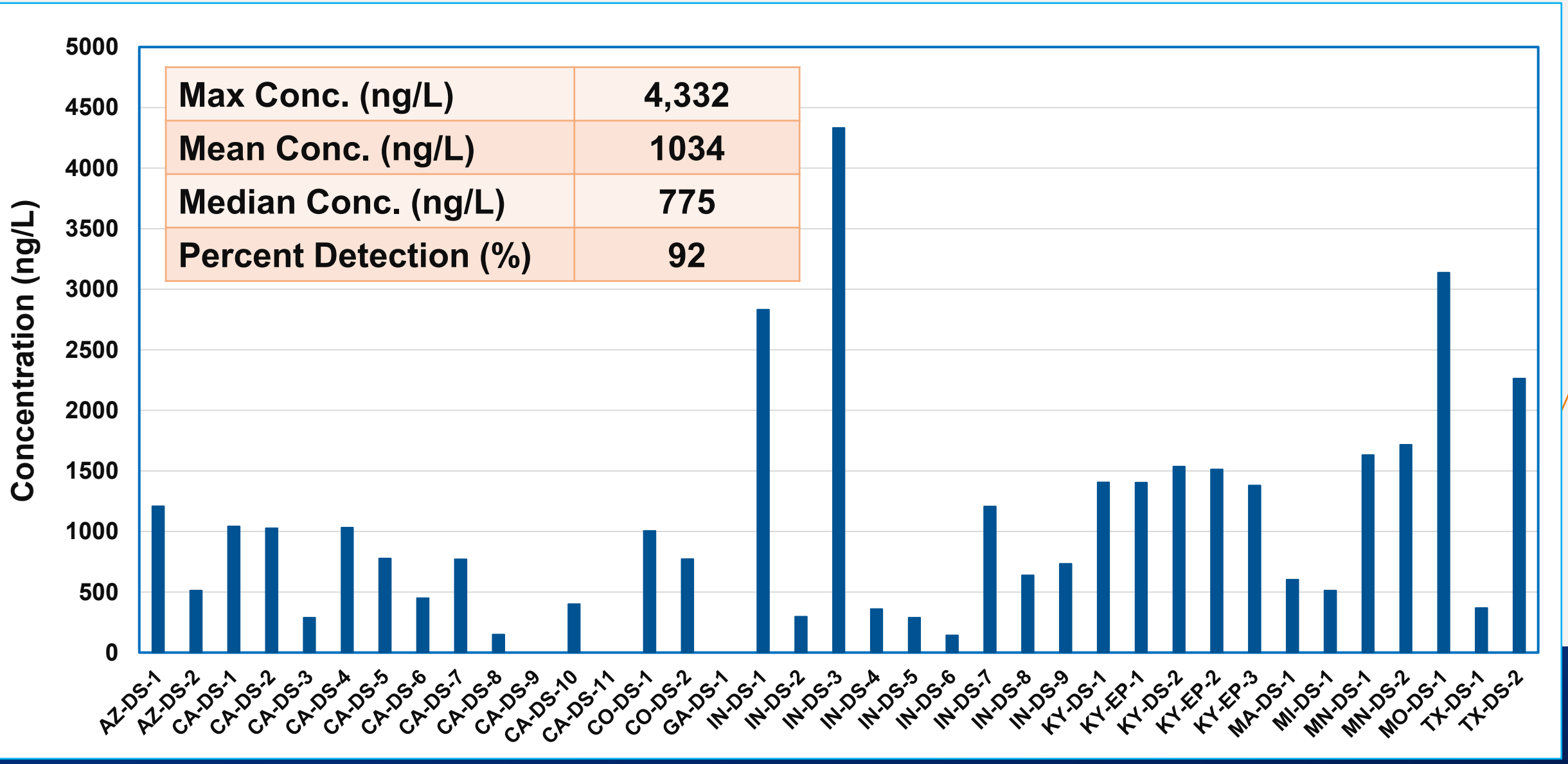
Matrix Spike Recoveries



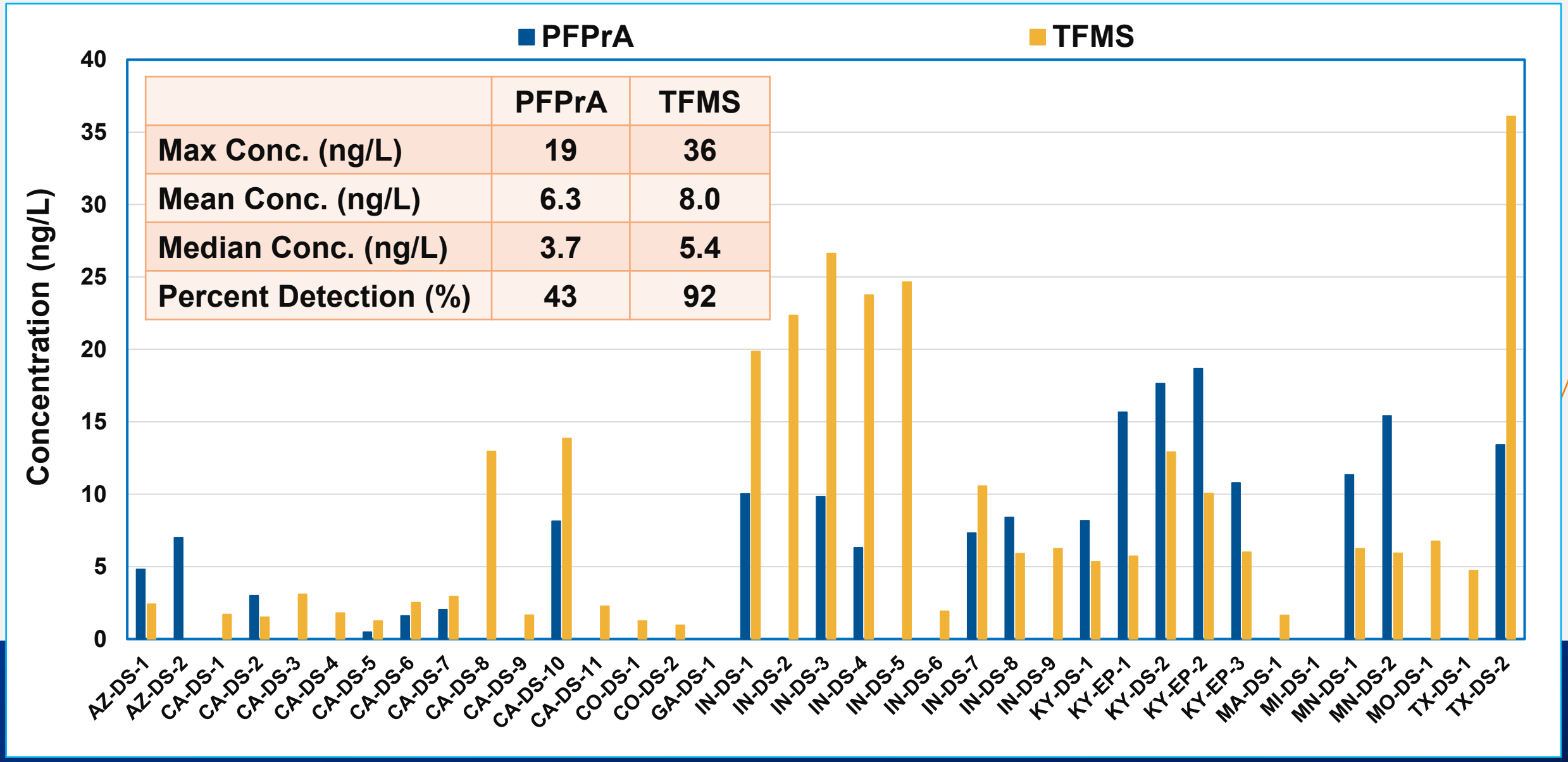
FS Results – IS Recoveries



FS Results – TFA

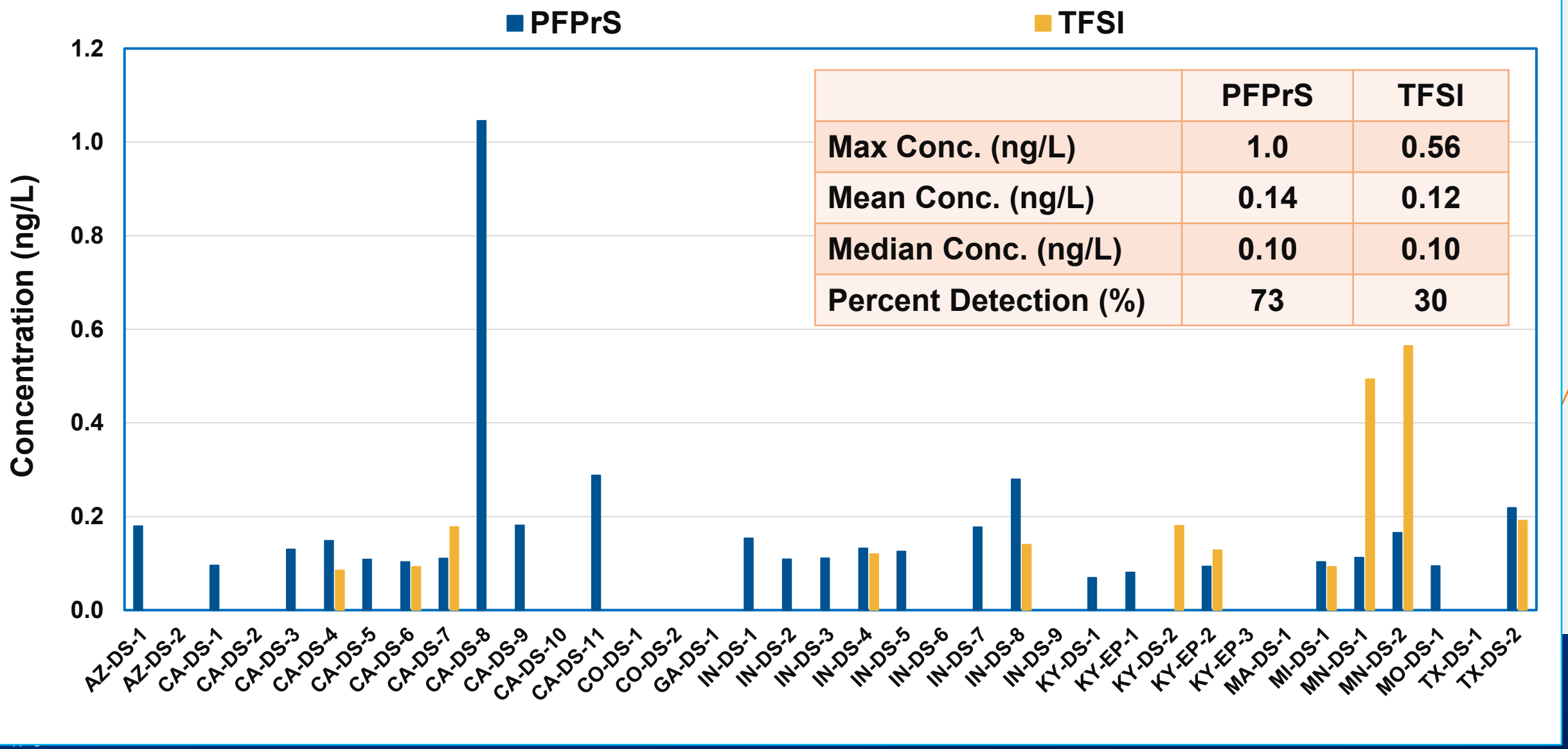


FS Results – PFPrA & TFMS



	PFPrA	TFMS
Max Conc. (ng/L)	19	36
Mean Conc. (ng/L)	6.3	8.0
Median Conc. (ng/L)	3.7	5.4
Percent Detection (%)	43	92

FS Results – PFPrS & TFSI



	PFPrS	TFSI
Max Conc. (ng/L)	1.0	0.56
Mean Conc. (ng/L)	0.14	0.12
Median Conc. (ng/L)	0.10	0.10
Percent Detection (%)	73	30

Conclusions

- A fast and sensitive DAI-LC/MS/MS method was demonstrated for analysis of ultrashort-chain PFAS in drinking water.
- The impacts of matrix interferences, particularly common anions, were minimum for the measurement of these C1-C3 PFAS except 2,3,3,3-TFPrA and 2,2,3,3-TFPrA. High concentration chloride and phosphate could seriously affect the detection of these two analytes.
- The detection rates of drinking water samples were: 92% (TFA & TFMS) > 73% (PFPrS) > 43% (PFPrA) > 30% (TFSI) > 0% (PFMOAA, PFEtS, 2,3,3,3-TFPrA & 2,2,3,3-TFPrA.
- The maximum concentrations were 4,332 ng/L for TFA, 36 ng/L for TFMS, and 19 ng/L for PFPrA, respectively.

Yongtao (Bruce) Li
Yongtao.Li@ET.EurofinsUS.com
574.472.5562

THANK YOU

eurofins | Environment Testing