SANITATION DISTRICTS OF LOS ANGELES COUNTY

Evaluation of QuEChERS Clean-up Sorbents for the Analysis of PFAS in Tissues and Biosolids

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Outline

- Introduction
- PFAS Methods – solid matrices
- QuEChERS for PFAS
- Method Performance
- Conclusion

ENVIRONMENTAL Science & Technology

Feature

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A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

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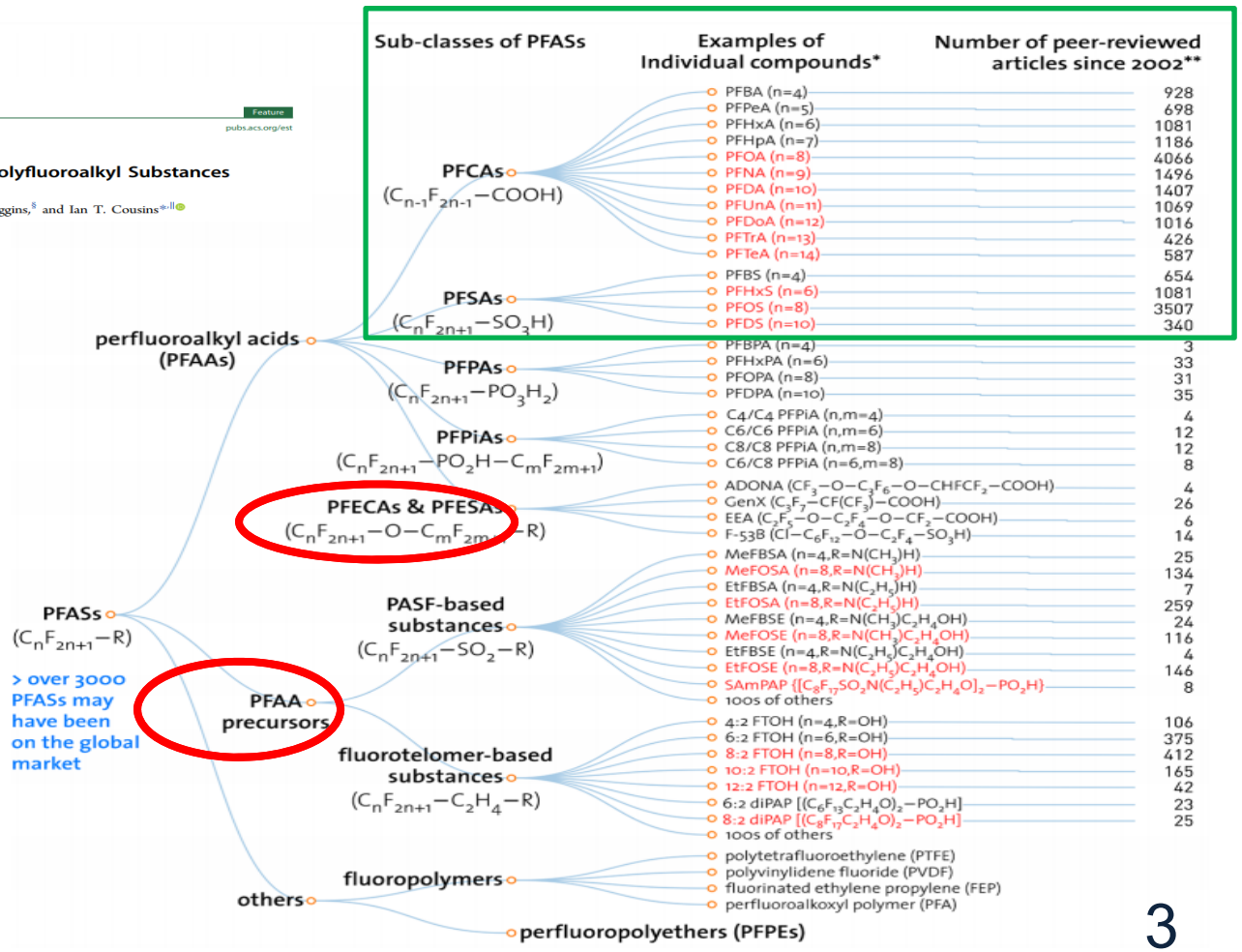


Why are we interested?

- ubiquitous; recalcitrant
- documented and potential health and environmental effects
- not removed by conventional WW treatment

Why are we interested?

- Potential regulation in CA
  - 70 ppt health advisory & 13/14 ppt NLs
- CA State Water Board Phased PFAS Investigation – LF, WRPs, **biosolids**
- LACSD fish monitoring programs

Solid Matrix PFAS Methods

	ASTM D7968	EPA-821-R-11-007	537Ms / DoD
Matrix	soils	sludge, biosolids	soil, sediments, biosolids, tissues, etc.
RL (ng/g)	0.025 - 0.75	0.25 - 10	var
prep method	SLE (rotator) centrifuge, filter	digestion, incubation, SLE (shake), SPE	var
clean-up	filtration	SPE WAX + filtration	var

SLE = Solid-Liquid Extraction
SPE = Solid Phase Extraction
WAX = Weak Anion Exchange

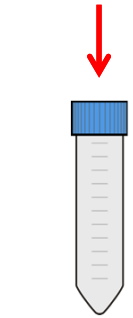
LACSD Solids PFAS Method

- validated for marine and river sediments for 17 PFAS compounds and 30+ CECs
- RL @ 0.25 ng/g based on 2 g sample
- being developed for PFAS/other CECs in tissues and biosolids; not yet validated
- QuEChERS method

QuEChERS

- Quick, Easy, Cheap, Effective, Rugged, and Safe
- developed for pesticide residue analysis in food
- solid-liquid micro-extraction followed by dispersive SPE (dSPE) clean up

Sample Preparation



2 g and
(MB & LCS)

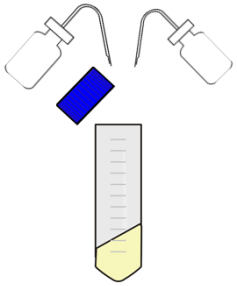
Air-dry (3-5 days)

2 g biosolids

4 g fish tissue

- spike with internal and QC standards; mix
- allow samples to equilibrate overnight
- freeze-dried samples recommended

Sample Extraction

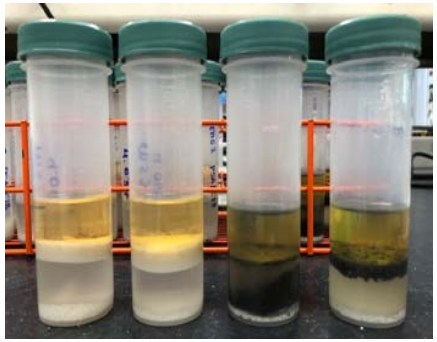


1. Add 10 mL H2O and 10 mL ACN

2. Add extraction salts (Phe rOQ QuEChERS AOAC 2007.01 salts)

3. Vortex for 1 minute

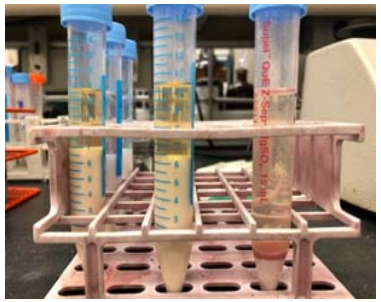
4. Centrifuge at 3500 rpm for 15 min



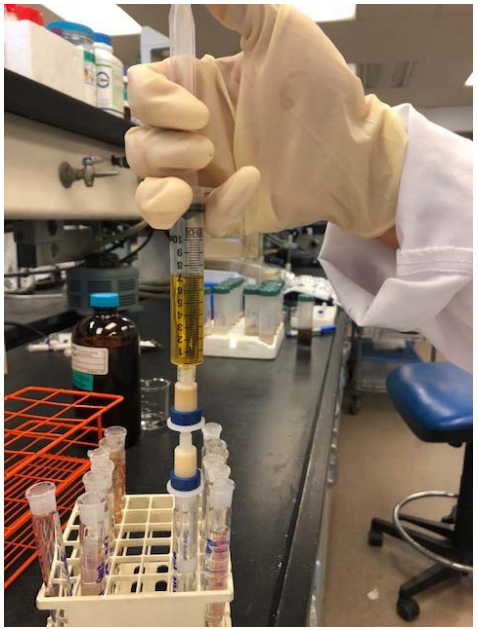
Sample Cleanup

dSPE

Transfer extract into a dSPE tube



Cartridge



Clean-up Sorbents

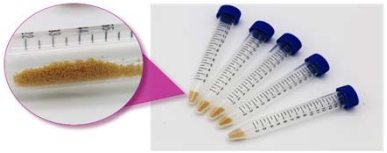
Phe PSA/C18

Sigma zSEP+

Agilent EMR

Phe Strata-X

Phe GCB



Phe LipoNo

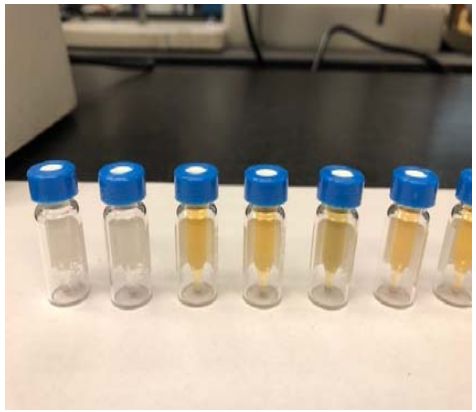
Oasis HLB

UCT LipiFiltr

Phe Phree

Sample Analysis

Dilute extracts 1:1 w/ DI H2O



Column: **Phenomenex Gemini C18 – 100 mm x 2.0 mm, 3 µm**

Delay Column: **Oasis WAX – 30 mm x 3.1, 3 µm**

Detector: **SCIEX 5500 QTRAP in sMRM mode**

Quantitation: **Isotope Dilution / IS**

Method Performance Criteria

	Clean up Method	
PFAS Compounds	LCS	70-130%
	Spikes	70-130%
	IS	50-150%
	RSD	20%

% Recovery – LCS (Sand)

	No cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo
PFPeA	101	96	94	79	96	99	108	106	102	97
PFHxA	98	104	100	111	98	99	105	108	102	100
PFHpA	96	91	96	97	92	93	108	106	99	98
PFOA	90	100	106	108	111	106	112	112	99	99
PFNA	101	80	82	81	102	106	99	97	99	98
PFDA	109	92	80	85	95	98	102	117	101	97
PFUdA	98	94	88	98	95	104	104	94	98	99
PFDoA	95	91	91	88	94	90	105	100	97	99
PFTrA	121	90	97	96	105	111	101	107	114	93
PFTeDA	102	87	99	91	99	102	111	110	99	95
PFBS	89	102	103	89	97	97	103	105	85	89
PFPeS	99	97	95	134	99	102	110	102	84	92
PFHxS	94	90	89	81	87	92	87	90	84	85
PFHpS	94	92	90	102	92	95	102	104	82	84
PFOS	96	94	90	97	93	98	95	98	100	95
PFNS	89	83	85	106	90	87	92	96	91	88
PFDS	90	95	92	118	89	89	88	92	89	88

$\bar{x}$ % Spike Recovery – Fish (n=3)

	No cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo
PFPeA	89	96	95	103	91	89	99	98	173	145
PFHxA	90	118	102	186	107	91	100	125	163	81
PFHpA	100	89	94	83	97	96	96	92	96	98
PFOA	91	95	91	99	87	100	95	92	94	94
PFNA	84	90	88	84	97	98	97	87	97	97
PFDA	94	81	88	80	85	89	100	107	93	92
PFUdA	96	98	94	95	104	107	103	101	95	94
PFDoA	95	95	86	91	97	94	101	99	94	92
PFTrA	100	115	98	89	117	122	109	88	111	96
PFTeDA	101	87	91	88	99	100	109	105	99	101
PFBS	93	109	106	100	91	90	113	97	81	86
PFPeS	104	105	104	144	109	106	114	118	91	88
PFHxS	90	91	91	83	92	90	100	97	80	82
PFHpS	97	92	96	106	100	96	109	109	86	89
PFOS	101	95	90	122	100	103	106	100	95	96
PFNS	95	92	88	95	94	98	102	99	89	91
PFDS	85	100	96	113	88	91	94	92	88	93

% RSD – Fish (n=3)

	No cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo
PFPeA	3	4	3	5	0.3	5	3	2	9	4
PFHxA	8	4	2	10	9	2	3	5	5	5
PFHpA	0.3	6	4	5	3	5	3	3	0.1	1
PFOA	11	4	6	5	4	5	13	6	0.2	1
PFNA	16	2	6	10	8	7	6	2	3	1
PFDA	2	4	4	3	6	2	5	4	3	2
PFUdA	1	5	8	4	7	12	8	8	2	1
PFDoA	1	8	8	7	7	6	9	12	2	1
PFTrA	3	3	9	5	4	6	12	9	2	1
PFTeDA	10	6	2	2	2	5	3	4	5	1
PFBS	0.2	3	3	2	3	4	1	2	4	2
PFPeS	6	6	2	3	3	4	6	4	5	1
PFHxS	0.2	3	1	3	2.5	3	2	2	3	2
PFHpS	2	3	2	3	1	3	4	2	3	1
PFOS	4	5	6	6	2	2	3	6	4	2
PFNS	1	4	1	4	1	4	3	5	7	3
PFDS	2	10	4	3	3	3	2	4	2	1


PARTY

$\bar{x}$ IS% Recovery – Sand (n=2)

	no cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata-X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo
PFPeA-IS	112	56	100	5	105	110	110	33	100	107
PFHxA-IS	112	61	103	8	103	113	123	40	107	120
PFHpA-IS	117	69	112	14	106	122	130	44	121	136
PFOA-IS	121	67	102	23	105	119	128	60	103	113
PFNA-IS	101	71	103	37	94	129	141	61	117	138
PFDA-IS	108	75	114	56	105	120	132	70	110	137
PFUdA-IS	110	80	109	71	103	117	136	69	104	133
PFDoa-IS	105	88	111	76	102	122	138	67	94	120
PFTeDA-IS	93	90	118	91	92	99	123	67	81	131
PFBS-IS	117	109	111	34	105	116	118	104	126	137
PFHxS-IS	121	117	129	60	110	128	132	112	128	151
PFOS-IS	116	111	115	66	105	127	136	120	113	136

$\bar{x}$ IS% Recovery – Fish (n=4)

	no cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata-X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo
PFPeA-IS	107	26	87	5	76	106	90	44	71	81
PFHxA-IS	112	29	95	8	80	110	100	51	69	79
PFHpA-IS	114	33	106	16	84	114	111	58	77	90
PFOA-IS	121	33	101	26	88	114	111	70	76	89
PFNA-IS	124	35	112	39	92	121	122	83	96	112
PFDA-IS	127	40	114	59	98	129	116	82	94	114
PFUdA-IS	121	43	117	75	92	126	120	89	101	121
PFDoa-IS	105	40	103	78	85	115	104	92	96	125
PFTeDA-IS	73	36	58	95	63	77	90	84	80	120
PFBS-IS	120	49	117	32	89	122	106	111	108	126
PFHxS-IS	130	56	131	62	100	136	118	126	116	136
PFOS-IS	130	53	129	69	101	134	118	134	113	129

$\bar{x}$ IS% Recovery – Biosolids (n=3)

	no cleanup	Phe PSA/C18	Supelco zSEP+	Agilent EMR	Phe Strata-X	Phe Phree	Waters HLB	UCT LipiFiltr	Phe GCB	Phe LipoNo	*Diluted - no cleanup (n=1)*
PFPeA-IS	60	19	81	12	59	57	53	44	64	77	101
PFHxA-IS	86	21	86	13	61	61	51	51	69	83	107
PFHpA-IS	87	25	95	21	66	69	81	58	72	89	116
PFOA-IS	81	21	87	82	37	66	70	70	67	83	106
PFNA-IS	38	27	94	108	73	34	77%	83	73	82	124
PFDA-IS	44	29	106	116	67	58	66	82	74	94	125
PFUdA-IS	48	24	53	67%	44	26	24	89	49	53	81
PFDoa-IS	29	19	81	43	18	13	11	92	34	31	54
PFTeDA-IS	21	19	12	19	15	9	4	84	15	22	25
PFBS-IS	117%	72%	130	124	91	124	288	111	91	116	128
PFHxS-IS	128%	81%	129	111	87	112	133	126	98	146	136
PFOS-IS	26	81%	141	176	44	0	214	134	88	94	121

Method Development – Phase 2

- add more PFAS compounds (CA list +)
- focus on clean up w/ decent performance
  - zSEP+, LipoNo
  - GCB (?)
  - drop filter format – solvent waste
- optimize compounds; validate

Conclusions

- QuEChERS is an effective extraction method for PFAS analysis (economical & less solvent waste)

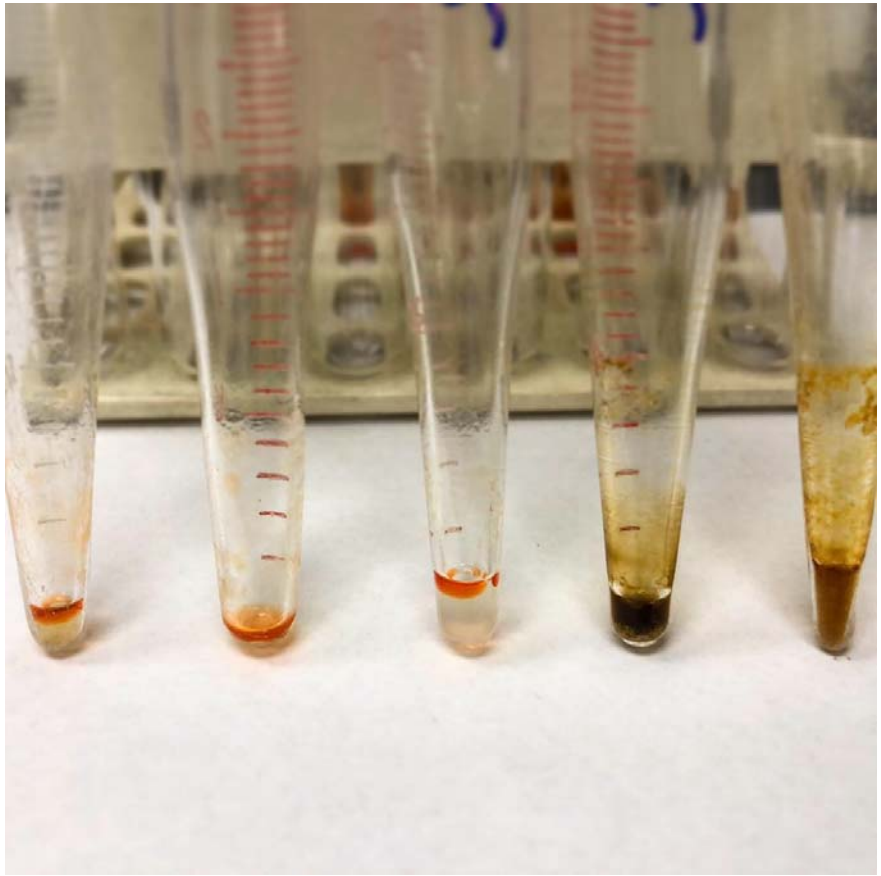
	ASTM D7968	EPA-821-R-11-007	LACSD QuEChERS
solvent/sample	10 mL	15 mL	**10 mL**
Estimated Prep Time (10 samples)	1.5 h	19.5 h	**1 h**

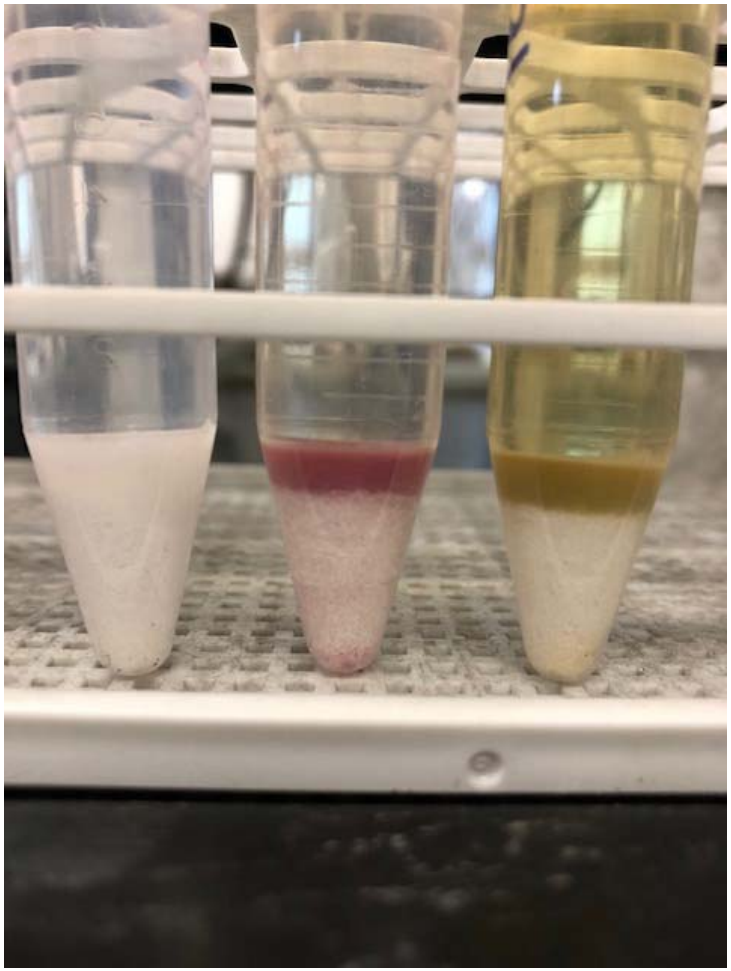
- Excellent recoveries and precision

Conclusions

- do not rely on isotope-dilution to compensate for a bad method
- be wary of data showing excellent recoveries for everything

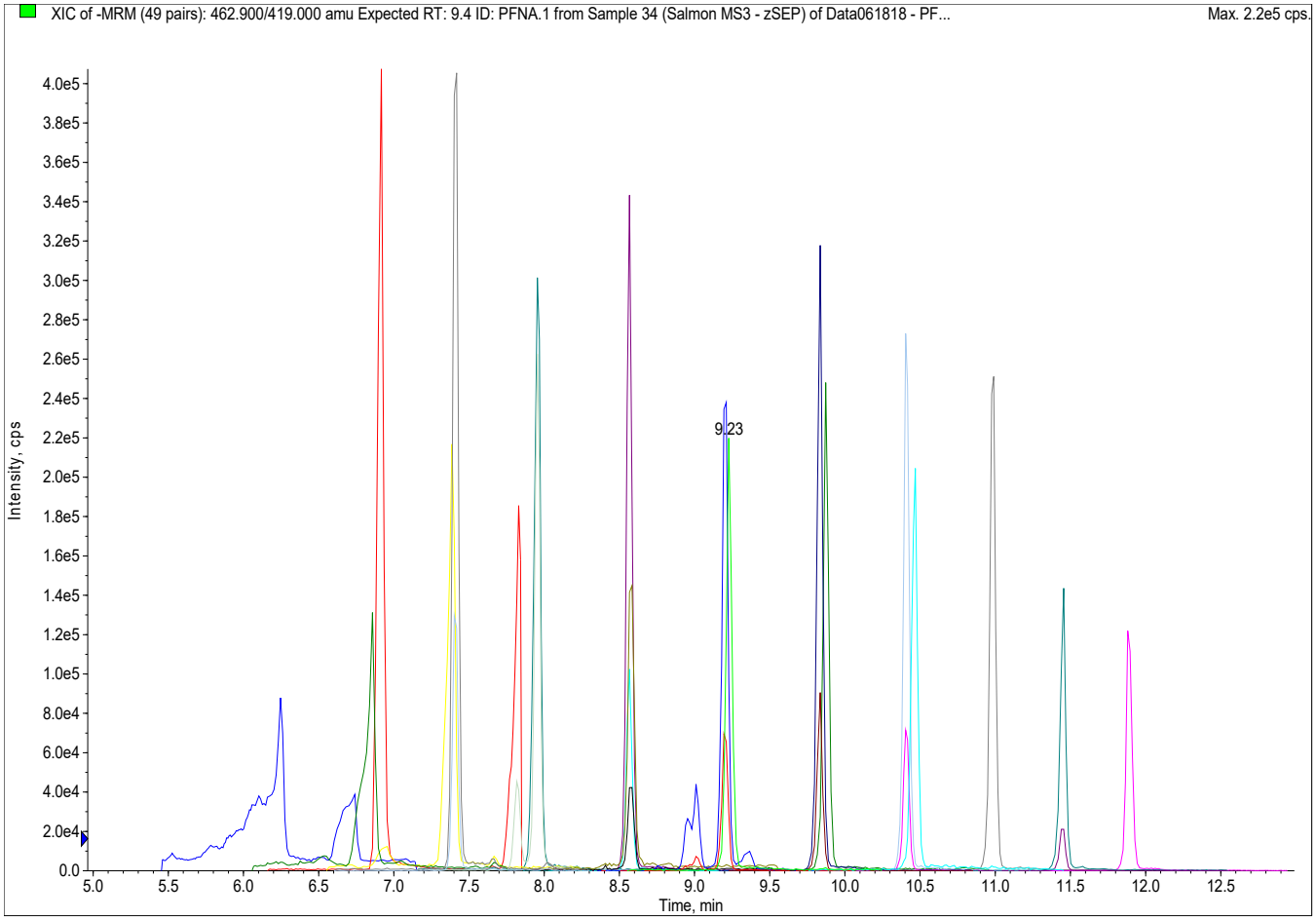
MISC. SLIDES





Cleanup	MB PFOA (ng/L)
No cleanup	3.74
Phe PSA/C18	4.43
Supelco zSEP+	5.32
Agilent EMR	9.91
Phe Strata-X	6.45
Phe Phree	6.46
Phe GCB	0
Waters HLB	9.91
UCT Lipifiltr	51.9
Phe LipoNo	4.16

- All MB PFOA < 1/5 RL except Lipifiltr
- All other PFAS MB = ND


XIC of -MRM (49 pairs): 462.900/419.000 amu Expected RT: 9.4 ID: PFNA.1 from Sample 34 (Salmon MS3 - zSEP) of Data061818 - PF...
Max. 2.2e5 cps.
Intensity, cps
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3.8e5
3.6e5
3.4e5
3.2e5
3.0e5
2.8e5
2.6e5
2.4e5
2.2e5
2.0e5
1.8e5
1.6e5
1.4e5
1.2e5
1.0e5
8.0e4
6.0e4
4.0e4
2.0e4
0.0
9.23
5.0
5.5
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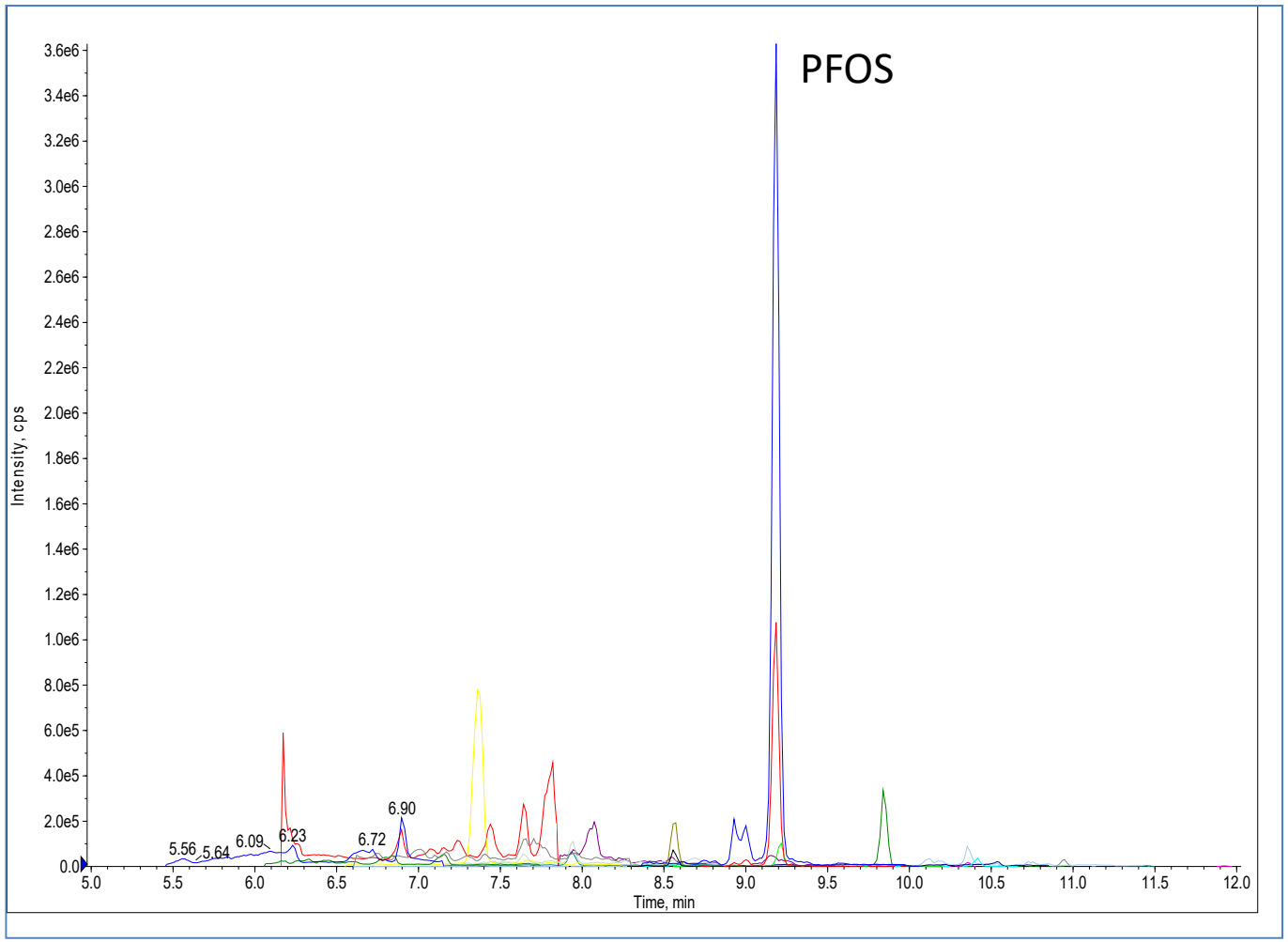
12.0
12.5
Time, min


PFOS
Intensity, cps
Time, min
3.6e6
3.4e6
3.2e6
3.0e6
2.8e6
2.6e6
2.4e6
2.2e6
2.0e6
1.8e6
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12.0
5.56
5.64
6.09
6.23
6.72
6.90