A NEW METHOD FOR THE ANALYSIS OF PFAS IN NON-POTABLE WATER

PRESENTED BY LAWRENCE ZINTEK

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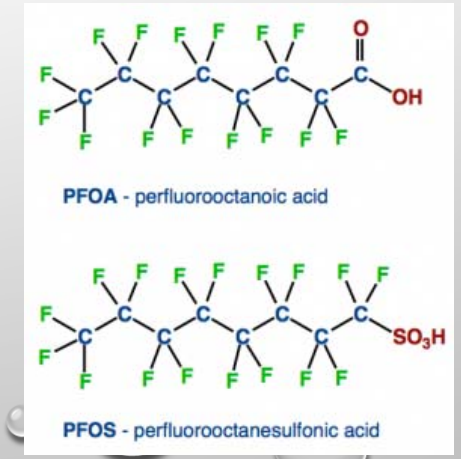
PFC BACKGROUND

- COMPOUNDS MANUFACTURED TO MAKE PRODUCTS MORE RESISTANT TO STAINS, GREASE, AND WATER
- FOUND IN:
  - FOAMS USED FOR FIRE SUPPRESSION
  - NON-STICK COOKWARE
  - WATERPROOF CLOTHING
  - STAIN-RESISTANT FABRICS
- MOST COMMON PFCS:
  - PERFLUOROOCTANOATE (PFOA)
  - PERFLUOROOCTYL SULFONATE (PFOS)



EXPANDED PFAS LIST

- NEED FOR AN EXPANDED PFAS LIST
  - ASTM D7979 -24 ANALYTES, 19 ISOTOPES/SURROGATES
  - UPDATED LIST CONTAINS 44 PFAS AND 24 ISOTOPES/SURROGATES
- NEED FOR A ROBUST QUICK DEFINITIVE METHOD WITH MINIMAL SAMPLE PREPARATION
- MANY LABORATORIES DO NOT HAVE THE STAFF TO CONDUCT LABORIOUS SAMPLE PREPARATION AND ANALYSIS PROCEDURES
- VALIDATED USING NINE WASTEWATER MATRICES AT THREE CONCENTRATIONS, EACH IN TRIPLICATE, SPANNING THE CALIBRATION RANGE

PFAS TARGET LIST

Analyte Name	Acronym	CAS Number	MDL (ng/L)	Range (ng/L)
Perfluorotetradecanoic acid	PFTreA	376-06-7	8.2	10-400
Perfluorotridecanoic acid	PFTriA	72629-94-8	17.2	10-400
Perfluorododecanoic acid	PFDoA	307-55-1	6.6	10-400
Perfluoroundecanoic acid	PFUnA	2058-94-8	3.9	10-400
Perfluorodecanoic acid	PFDA	335-76-2	3.4	10-400
Perfluorononanoic acid	PFNA	375-95-1	5.2	10-400
Perfluorooctanoic acid	PFOA	335-67-1	2.5	10-400
Perfluoroheptanoic acid	PFHpA	375-85-9	5.9	10-400
Perfluorohexanoic acid	PFHxA	307-24-4	2.1	10-400
Perfluoropentanoic acid	PFPeA	2706-90-3	13	50-1000
Perfluorobutanoic acid	PFBA	375-22-4	17.1	50-1000
Perfluorodecanesulfonic acid	PFDS	335-77-3	1.6	10-400
Perfluorononanesulfonic acid	PFNS	68259-12-1	1.2	10-400
Perfluorooctanesulfonic acid	PFOS	1763-23-1	4.4	10-400
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	2.7	10-400
Perfluorohexanesulfonic acid	PFHxS	355-46-4	2.3	10-400
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	2.7	10-400
Perfluorobutanesulfonic acid	PFBS	375-73-5	3.3	10-400
Perfluorooctanesulfonamide	PFOSA	754-91-6	2.2	10-400
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4	4.5	10-400
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	2.7	10-400
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4	3.2	10-400

PFAS TARGET LIST CONTINUED

Analyte Name	Acronym	CAS Number	MDL	Range
			(ng/L)	(ng/L)
N-Ethylperfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	2.6	10-400
N-Methylperfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	1.3	10-400
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	2.2	10-400
N-Methylperfluorooctanesulfonamide	NMeFOSA	31506-32-8	2.1	10-400
N-Ethylperfluorooctanesulfonamide	NEtFOSA	4151-50-2	1.8	10-400
N-Methylperfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	3.1	10-400
N-Ethylperfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	2.7	10-400
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	3.7	10-400
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	2.1	10-400
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	2.7	10-400
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	2.2	10-400
Pentafluorpropanoic acid	PFPrA	422-64-0	20.3	50-1000
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	3.7	10-400
Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7	2.2	10-400
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	2.6	10-400
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	2.2	10-400
2H,2H,3H,3H-Perfluorohexanoic Acid	3:3 FTCA	356-02-05	3.7	10-400
2H,2H,3H,3H-Perfluorooctanoic Acid	5:3 FTCA	914637-49-3	3	10-400
2H,2H,3H,3H-Perfluorodecanoic acid	7:3 FTCA	812-70-4	1.5	10-400
2H-perfluoro-2-octenoic acid	FHUEA	70887-88-6	2.5	10-400
2H-perfluoro-2-decenoic acid	FOUEA	70887-84-2	2.9	10-400
Lithium Bis(trifluoromethane)sulfonimide	HQ-115	90076-65-6	9	10-400

SURROGATE/ISOTOPE LIST

Surrogate Name	Acronym
Perfluoro-n-[^{13}C4]butanoic acid	MPFBA
Perfluor0-n-[$^{13}C_5$]pentanoic acid	M5PFPeA
Perfluoro-n-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	M5PFHxA
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	M4PFHpA
Perfluoro-n-[$^{13}C_8$]octanoic acid	M8PFOA
Perfluoro-n-[$^{13}C_9$]nonanoic acid	M9PFNA
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	M6PFDA
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	M7PFUnA
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	MPFDoA
Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid	M2PFTreA
Perfluoro-1-[$^{13}C_8$]octanesulfonamide	M8FOSA
N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	D3-N-MeFOSAA
N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	D5-N-EtFOSAA
N-methyl-d_3-perfluoro-1-octanesulfanamide	d-N-MeFOSA
N-ethyl-d_5-perfluoro-1-octanesulfanamide	d-N-EtFOSA
2-(N-methyl-d_3-perfluoro-1-octanesulfonamido)ethan-d_4-ol	d7-N-MeFOSE
2-(N-ethyl-d_5-perfluoro-1-octanesulfonamido)ethan-d_4-ol	D9-N-EtFOSE
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-$^{13}C_3$-propanoic acid	MHFPO-DA
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]hexane sulfonate	M4:2FTS
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octane sulfonate	M6:2FTS
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate	M8:2FTS
Perfluoro-1-[$^{13}C_8$]octanesulfonate	M8PFOS
Perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	MPFBS
Perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonate	M3PFHxS

EXPANDED PFAS WATER METHOD

OVERVIEW

- DEVELOPED FOR NON-DRINKING WATER AQUEOUS SAMPLES (E.G. WASTEWATER, SLUDGE, INFLUENT, EFFLUENT)
- EXTERNAL STANDARD CALIBRATION:
  - 44 TARGET ANALYTES, 24 SURROGATES
- PREPARATION:
  - SAMPLE SIZE = 5 ML
  - SAMPLES DILUTED 1:1 WITH METHANOL, SHAKEN FOR 2 MINUTES, FILTERED THROUGH A POLYPROPYLENE MEMBRANE, AND ACIDIFIED WITH ACETIC ACID (PH ~3-4); 10 ML FINAL VOLUME
    - SLUDGE SAMPLES ARE ADJUSTED TO PH ~9-10 WITH AMMONIUM HYDROXIDE DURING PREPARATION, AFTER FILTERING ACIDIFY.
  - ANALYSIS BY LC/MS/MS (SAME CONDITIONS AS IN ASTM D7979)
    - REQUIRED TO HAVE ADEQUATE CHROMATOGRAPHY

SAMPLE COLLECTION WATER

- COLLECT A 5.0 ML SAMPLE, GRAB WOULD BE BEST, IN A GRADUATED 15 ML POLYPROPYLENE TUBE IN THE FIELD SO THAT THE WHOLE SAMPLE IS PROCESSED IN THE LAB (NO ALIQUOTING).
- FOR ACCURATE VOLUMES, THE WEIGHT OF THE 15 ML POLYPROPYLENE TUBE MAY BE TAKEN BEFORE AND AFTER SAMPLING IN ORDER TO GET AN EXACT VOLUME. THE DENSITY OF WATER IS ASSUMED TO BE 1.0 G/ML UNLESS THE EXACT DENSITY OF THE WATER SAMPLE IS KNOWN, THEN THAT CONVERSION SHOULD BE USED.

SPORADIC PFAS HITS

- STARTED ABOUT 2 YEARS AGO (COVID?)
- STRAY HITS IN CONSUMABLES (VIALS, PIPETTE TIPS, POLYPROPYLENE TUBES…)
- RESULT IS DIFFICULT TO ACHIEVE LOW PPT MDL DETERMINATION FOR SOME PFAS
- FALSE POSITIVES (USUALLY UP TO 30 NG/L)
- PFAS ARE WIDELY USED IN INDUSTRY IN MANY APPLICATIONS AND ARE COMMON
  - "THEY DON'T EVEN KNOW THEY ARE USING THEM"
- HOW WE ARE DEALING WITH IT
  - CHECKING SUPPLIES AND CHANGING VENDORS
  - IF YOU CHECK A LOT AND THE FEW COME OUT CLEAN DOES NOT MEAN THE WHOLE LOT IS CLEAN
  - ANALYZING ALL SAMPLES IN TRIPLICATE AND DETERMINING PRECISION AND IDENTIFYING FALSE POSITIVES

Sporadic Hit Example- PFTriA MDL

Compound	Results ng/L
perfluorotridecanoate	11
(10 ng/L Spike)	10.6
	21.3#
	10.6
	9.9
	10.7
	7.82
	11.1
	25.4#
Grubbs Outlier	55.5*
Average	13.2
Std. Deviation	5.951
MDL	17.2

Hardly ever found a "real" PFTriA hit in a site sample

SPORADIC HITS ARE NOT CARRY-OVER

- PFTriA Spike in (Bot2) Landfill Leachate and (Bot3) Metal Finisher Matrices
- Three unspiked per matrix, three spiked at 8 ng/L, 3 at 80 ng/L and 3 at 160 ng/L (Below Concentrations not corrected for Dilution)

Compound name: PFTRiA

	Inj. Name	Sample ID	RT (min.)	Pred. RT (min.)	RT Dev. (%)	Area	Std. Conc. (ppt)	Conc. (ppt)	Conc. Dev. (%)	S/N
1	060821RB1		10.168	10.180	-0.1	404				27
2	060821RB2		10.169	10.180	-0.1	359				18
3	060821Lev1		10.180	10.180	0.0	2530	5	4.93	-1.3	83
4	060821Lev2		10.185	10.180	0.1	4759	10	10.36	3.6	190
5	060821Lev3		10.196	10.180	0.2	8671	20	19.83	-0.8	427
6	060821Lev4		10.196	10.180	0.2	17194	40	40.23	0.6	708
7	060821Lev5		10.191	10.180	0.1	24322	60	57.06	-4.9	531
8	060821Lev6		10.196	10.180	0.2	34552	80	80.85	1.1	1318
9	060821Lev7		10.190	10.180	0.1	43333	100	100.94	0.9	759
10	060821Lev8		10.201	10.180	0.2	66581	150	152.79	1.9	984
11	060821Lev9		10.196	10.180	0.2	87538	200	197.98	-1.0	863
12	060821RB3		10.202	10.180	0.2	445				13
13	060821secsource		10.212	10.180	0.3	43373	100	101.03	1.0	1002
14	060821mb1	B21F002-BLK1	10.218	10.180	0.4	1104		1.45		18
15	060821mb2	B21F002-BLK2	10.213	10.180	0.3	412				13
16	060821mrl1	B21F002-MRL1	10.213	10.180	0.3	2111		3.91		90
17	060821mrl2	B21F002-MRL2	10.207	10.180	0.3	2793		5.57		80
18	060821lcs1	B21F002-BS1	10.213	10.180	0.3	32025		75.01		840
19	060821lcs2	B21F002-BSD1	10.212	10.180	0.3	34311		80.29		2925
20	060821RB4		10.207	10.180	0.3	412				15
21	060821Bot2mb1	2105014-01	10.218	10.180	0.4	673		0.39		16
22	060821Bot2mb2	2105014-01RE1	10.207	10.180	0.3	1164		1.60		35
23	060821Bot2mb3	2105014-01RE2	10.218	10.180	0.4	657		0.35		30
24	060821Bot2low1	B21F002-MS1	10.218	10.180	0.4	3318		6.85		124
25	060821Bot2low2	B21F002-MS2	10.212	10.180	0.3	3449		7.17		166
26	060821Bot2low3	B21F002-MS3	10.207	10.180	0.3	4124		8.82		67
27	060821Bot2mid1	B21F002-MS4	10.218	10.180	0.4	34323		80.32		738
28	060821Bot2mid2	B21F002-MS5	10.207	10.180	0.3	35035		81.96		3085
29	060821Bot2mid3	B21F002-MS6	10.212	10.180	0.3	33535		78.50		884
30	060821Bot2hi1	B21F002-MS7	10.207	10.180	0.3	61085		140.70		834
31	060821Bot2hi2	B21F002-MS8	10.213	10.180	0.3	65360		150.11		693
32	060821Bot2hi3	B21F002-MS9	10.212	10.180	0.3	67665		155.16		3877
33	060821Bot3mb1	2105015-01	10.207	10.180	0.3	740		0.56		13

REST OF RUN

- REAGENT BLANK RAN AFTER HIGH LEVEL SPIKE IN METAL FINISHER MATRIX, NO CARRY-OVER, FOLLOWED BY END CCV.

Compound name: PFTRiA

	Inj. Name	Sample ID	RT (min.)	Pred. RT (min.)	RT Dev. (%)	Area	Std. Conc. (ppt)	Conc. (ppt)	Conc. Dev. (%)	S/N
34	060821Bot3mb2	2105015-01RE1	10.179	10.180	-0.0	246				4
35	060821Bot3mb3	2105015-01RE2	10.174	10.180	-0.1	906		0.96		19
36	060821Bot3low1	B21F002-MSA	10.168	10.180	-0.1	3228		6.64		105
37	060821Bot3low2	B21F002-MSB	10.163	10.180	-0.2	3557		7.44		48
38	060821Bot3low3	B21F002-MSC	10.158	10.180	-0.2	3474		7.23		42
39	060821Bot3mid1	B21F002-MSD	10.147	10.180	-0.3	32622		76.39		613
40	060821Bot3mid2	B21F002-MSE	10.136	10.180	-0.4	31664		74.18		567
41	060821Bot3mid3	B21F002-MSF	10.136	10.180	-0.4	32663		76.49		934
42	060821Bot3hi1	B21F002-MSG	10.130	10.180	-0.5	63910		146.93		543
43	060821Bot3hi2	B21F002-MSH	10.125	10.180	-0.5	66002		151.52		857
44	060821Bot3hi3	B21F002-MSI	10.125	10.180	-0.5	63388		145.78		1459
45	060821RB5		10.113	10.180	-0.7	422				10
46	060821Lev5ccv		10.108	10.180	-0.7	25926	60	60.82	1.4	680

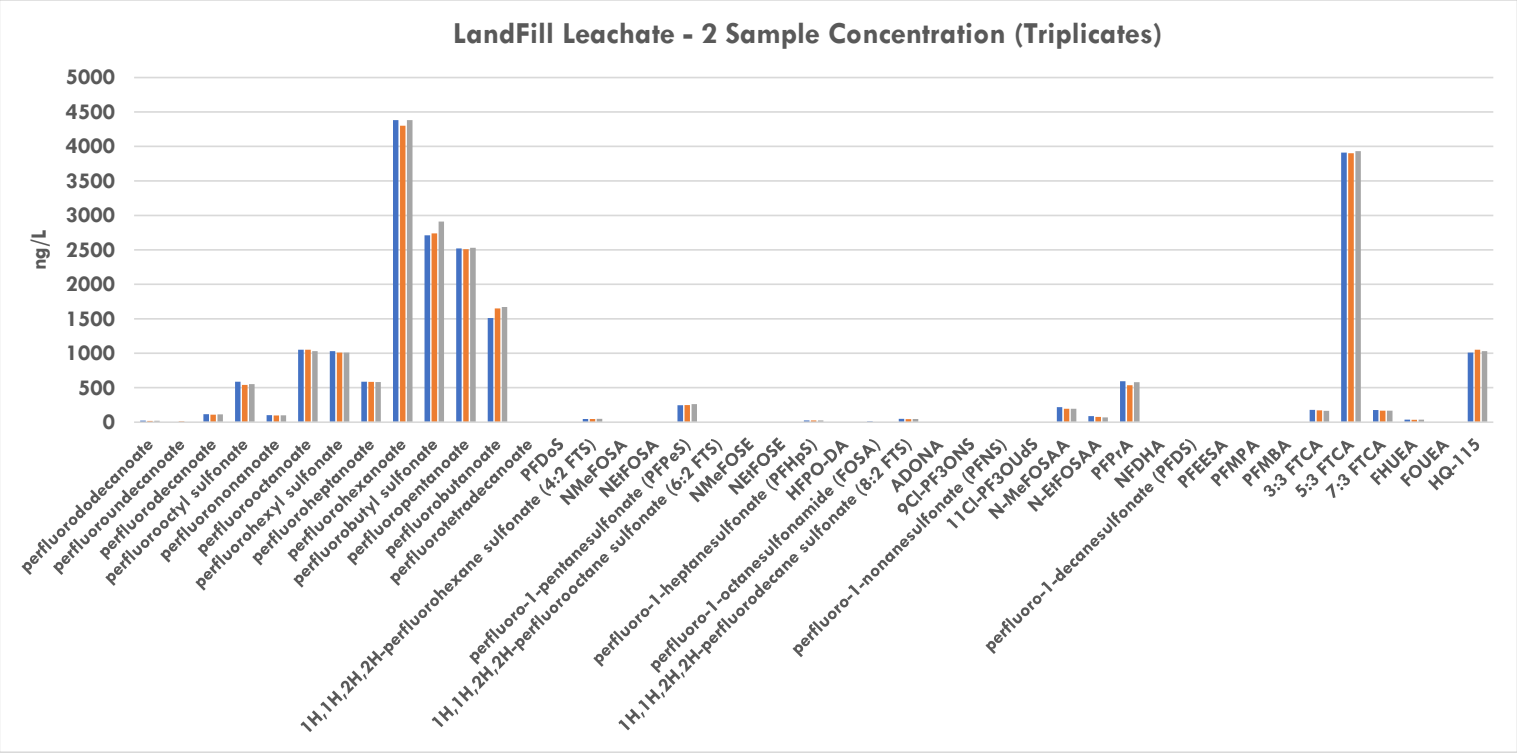
MATRICES USED FOR VALIDATION

- REAGENT WATER
- NINE WASTEWATER MATRICES FROM EPA OFFICE OF WATER
  - LANDFILL LEACHATE
  - METAL FINISHER
  - TWO POTW EFFLUENTS
  - HOSPITAL
  - POTW INFLUENT
  - BUS WASHING STATION
  - POWER PLANT
  - PULP AND PAPER EFFLUENT

MATRIX SPIKE LEVELS

- EACH MATRIX
  - THREE ANALYZED UNSPIKED
  - THREE ANALYZED SPIKED AT 16 NG/L (CONCENTRATION IN THE WATER SAMPLE)
  - THREE ANALYZED SPIKED AT 160 NG/L
  - THREE ANALYZED AT 320 NG/L
- SOME MATRIX SPIKES WERE WELL BELOW THE NATIVE PFAS FOUND IN THE MATRIX SAMPLES

LANDFILL LEACHATE UNSPIKED TRIPLICATE

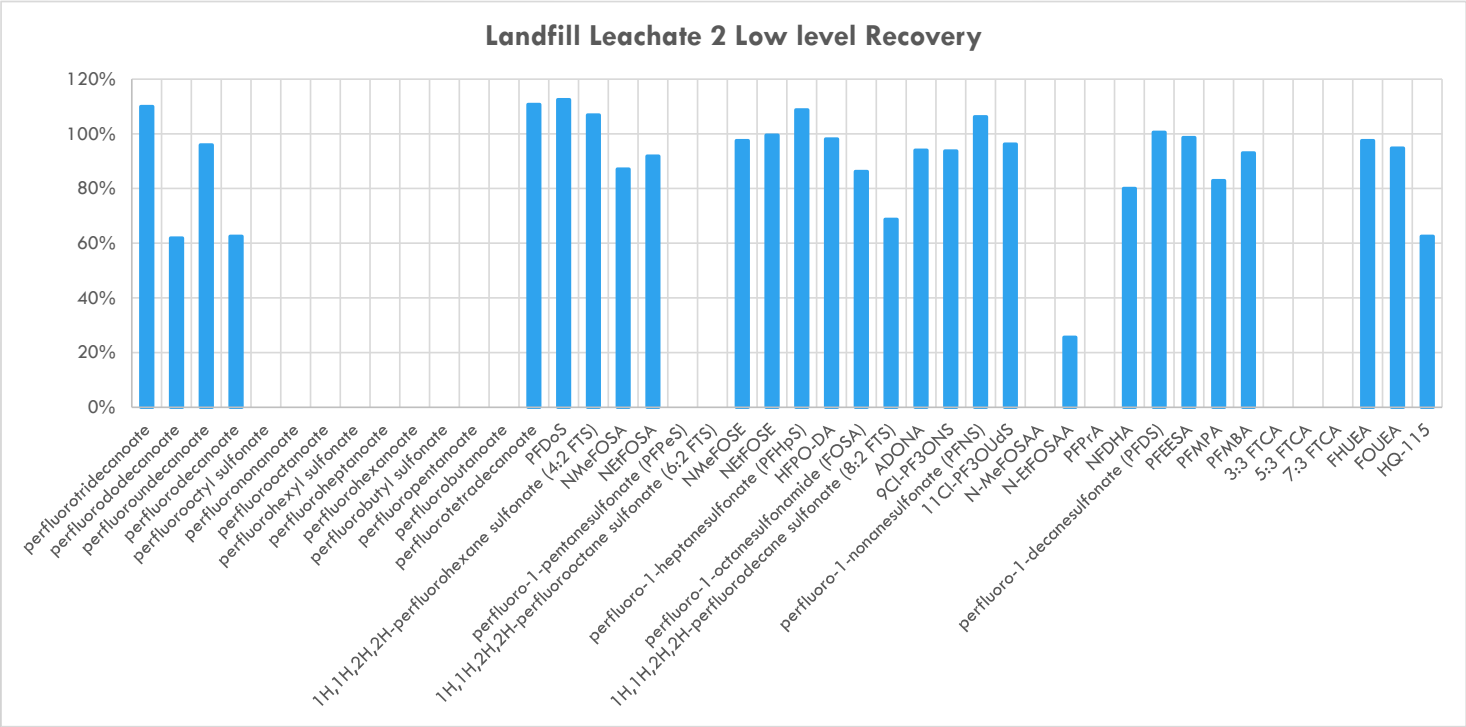


6:2 FTS not calculated- estimated to be at 300,000 ng/L

PFAS present- Excellent precision.

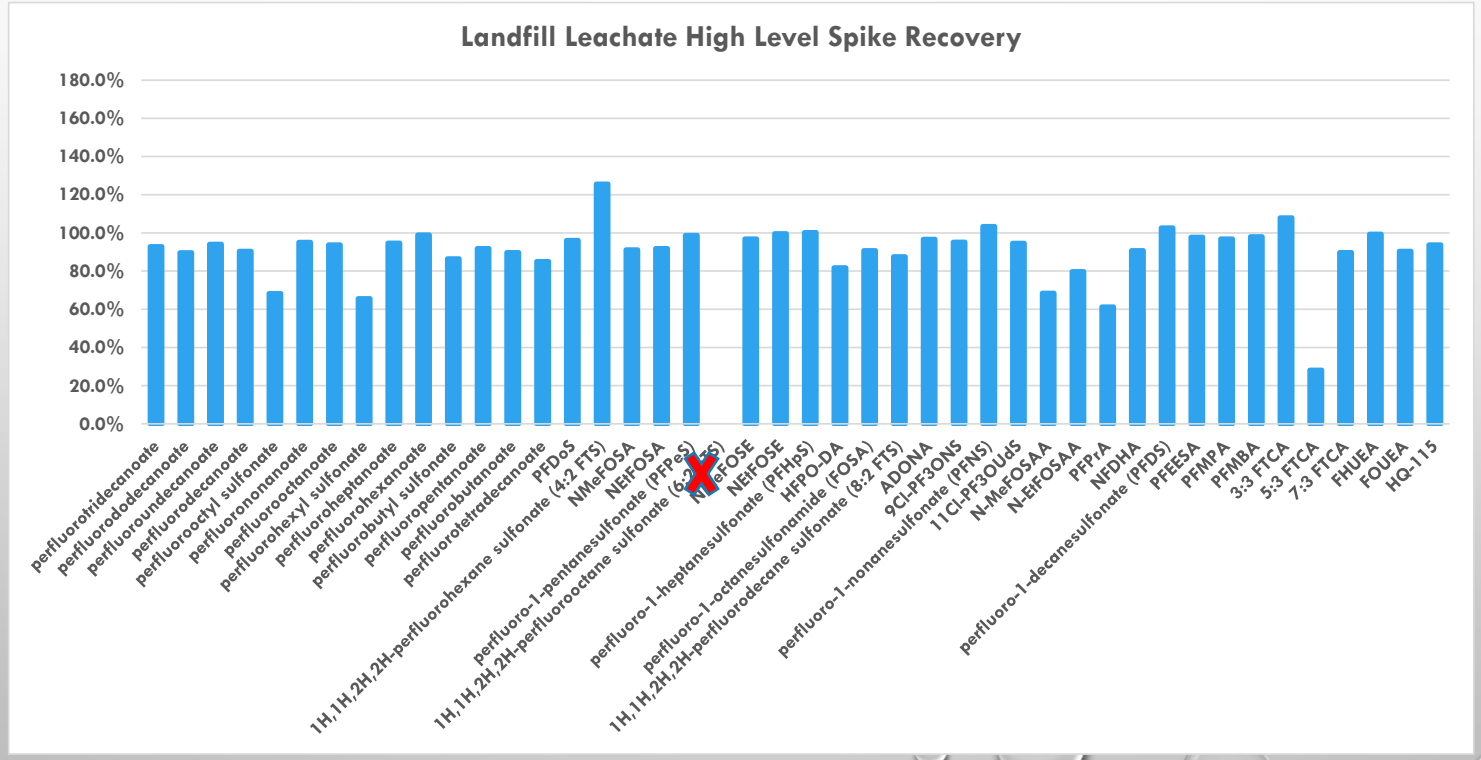
LANDFILL LEACHATE (16 NG/L SPIKE)

Many PFAS spikes **really** insignificant!

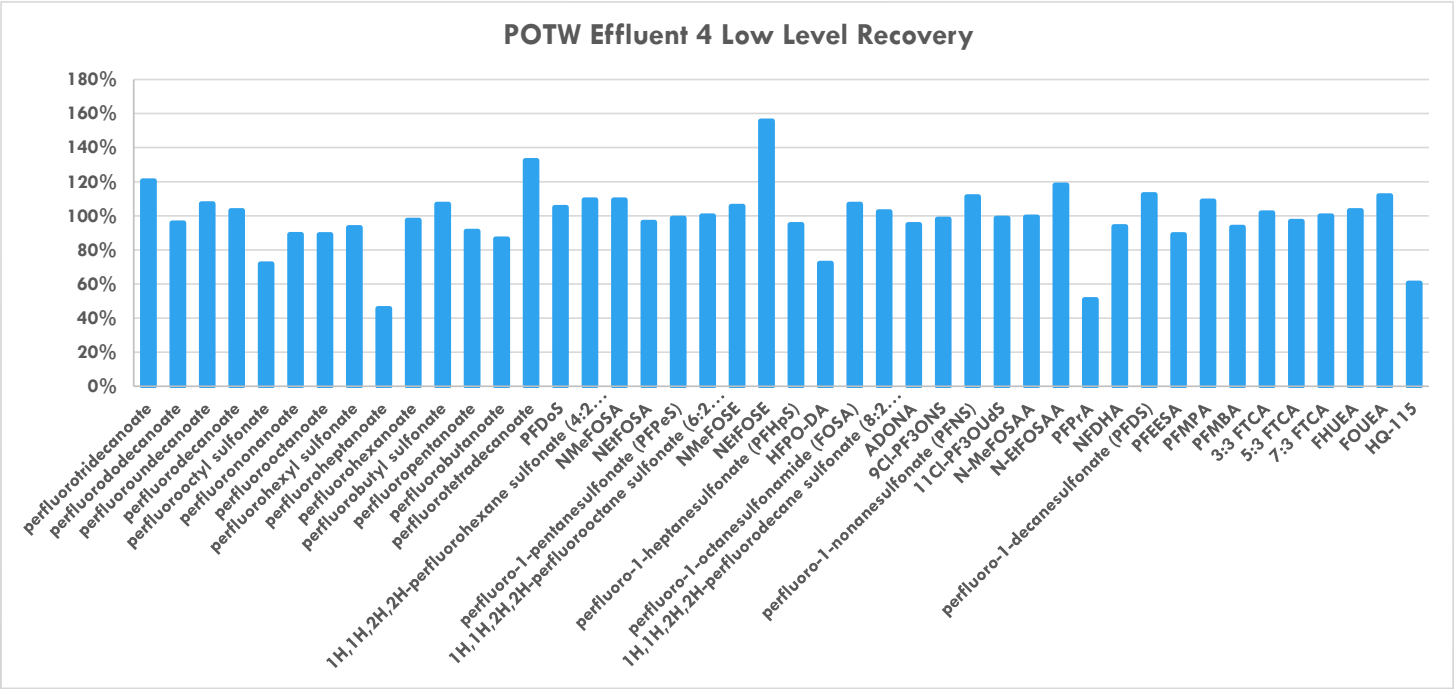


LANDFILL LEACHATE (320 NG/L SPIKE)

6:2 FTS spike **really** insignificant!

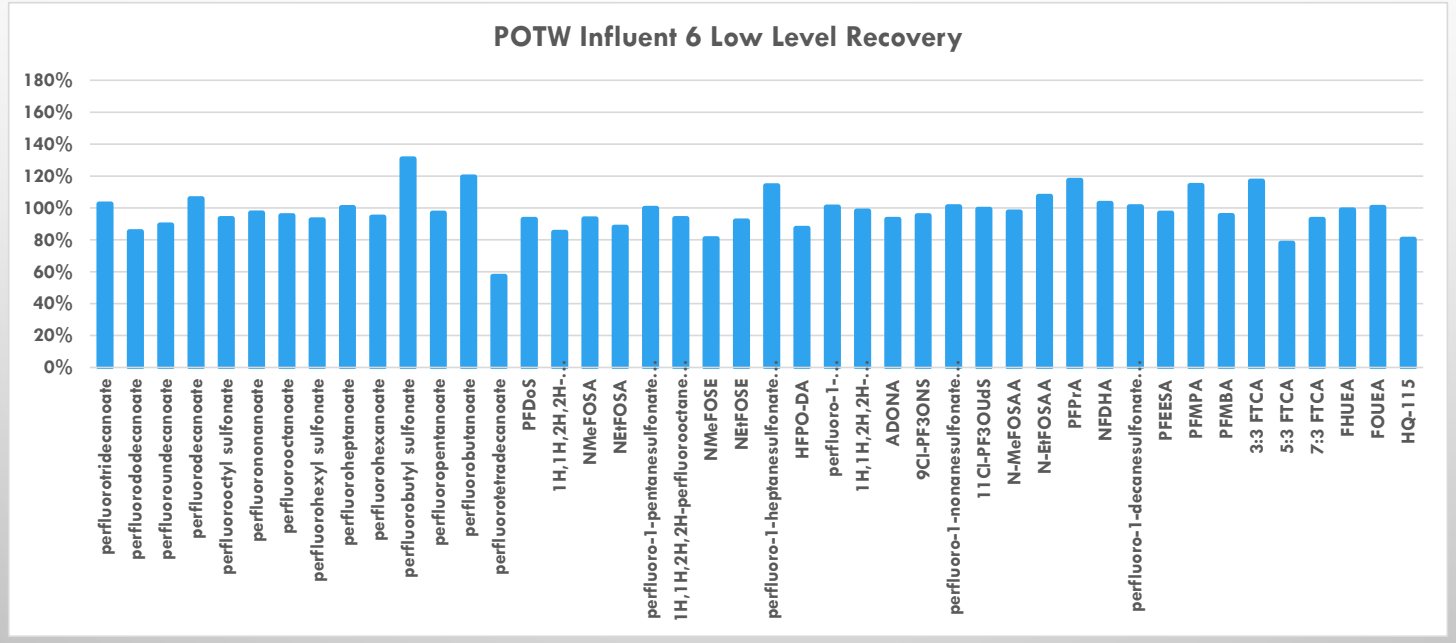


POTW EFFLUENT (16 NG/L SPIKE)



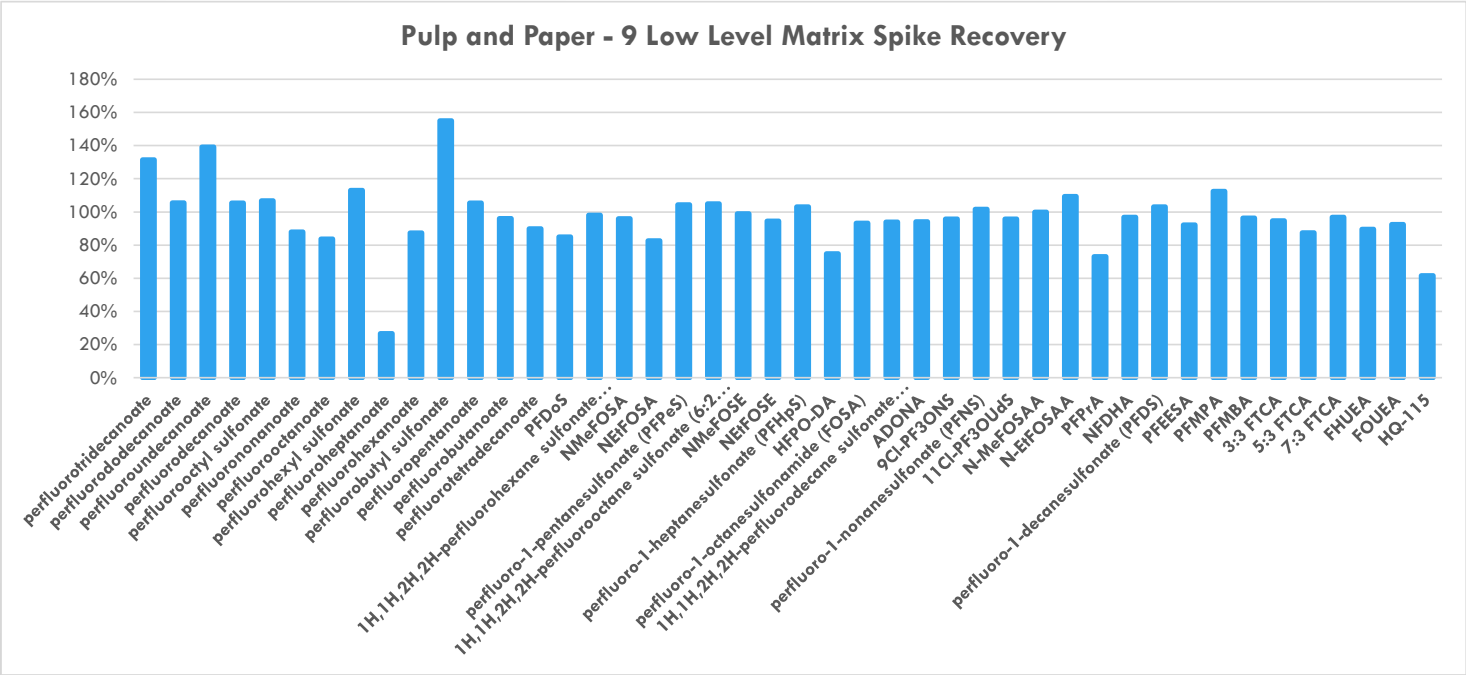
Everyone can show high spike recoveries, we showing the low.

POTW INFLUENT (16 NG/L SPIKE)



LW1

PULP AND PAPER MATRIX (16 NG/L)



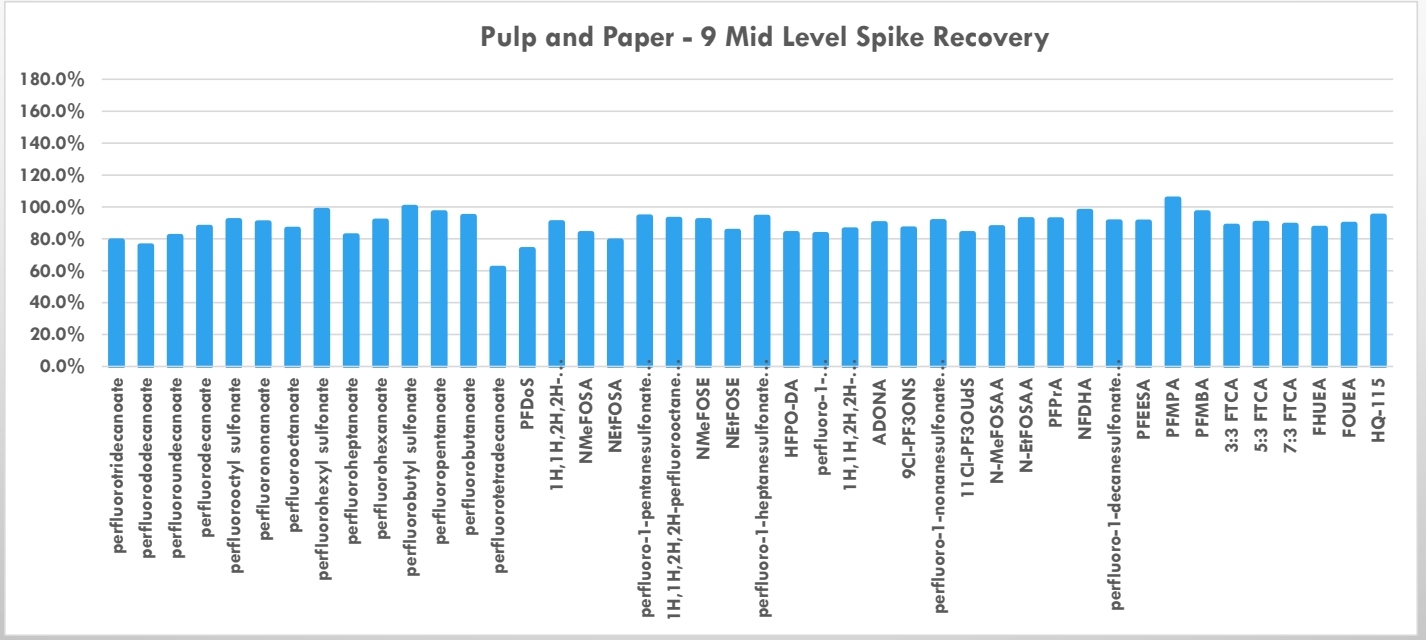
"Everybody" talks about pulp and paper being the decider if a method is acceptable

<u>These are all by EXTERNAL CALIBRATION!</u> NONE OF THIS IS BY ISOTOPE DILUTION.

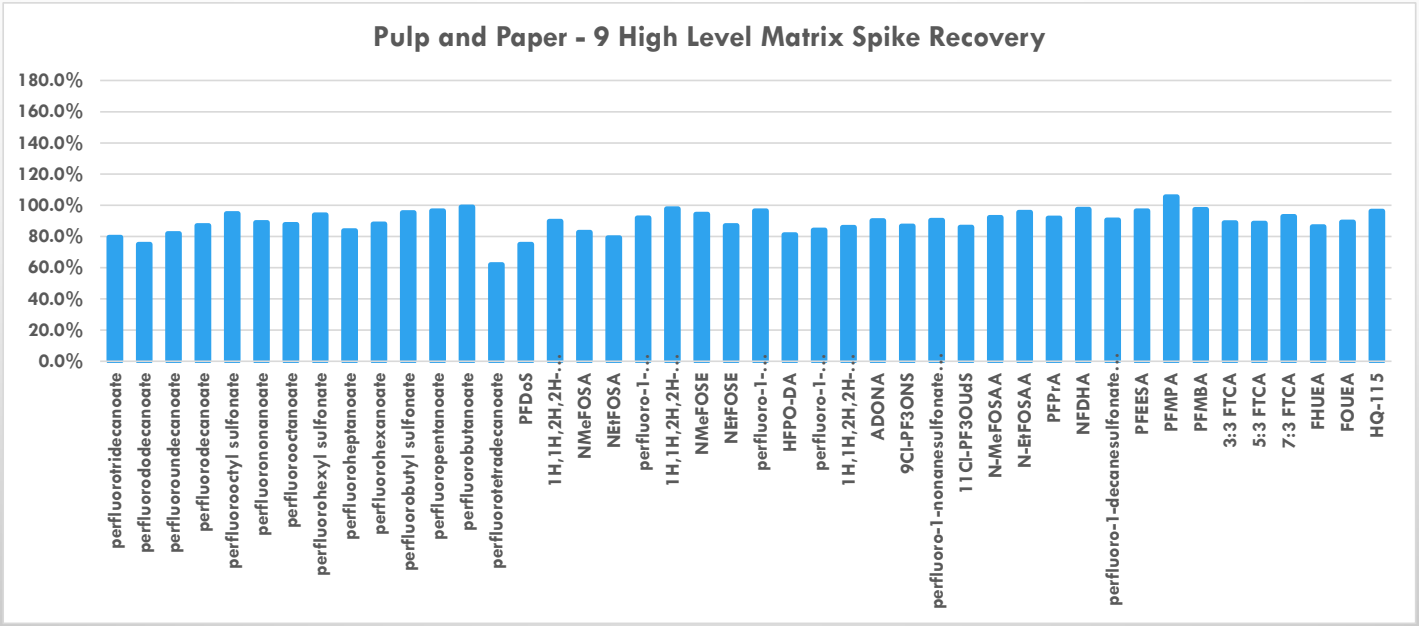
Slide 20

LW1 note, PFHxS, if this was isotope dilution this low recovery would be corrected up. But, the low recovery may provide researchers with valuble information. Why not report what we get?
Lipps, William, 7/15/2021

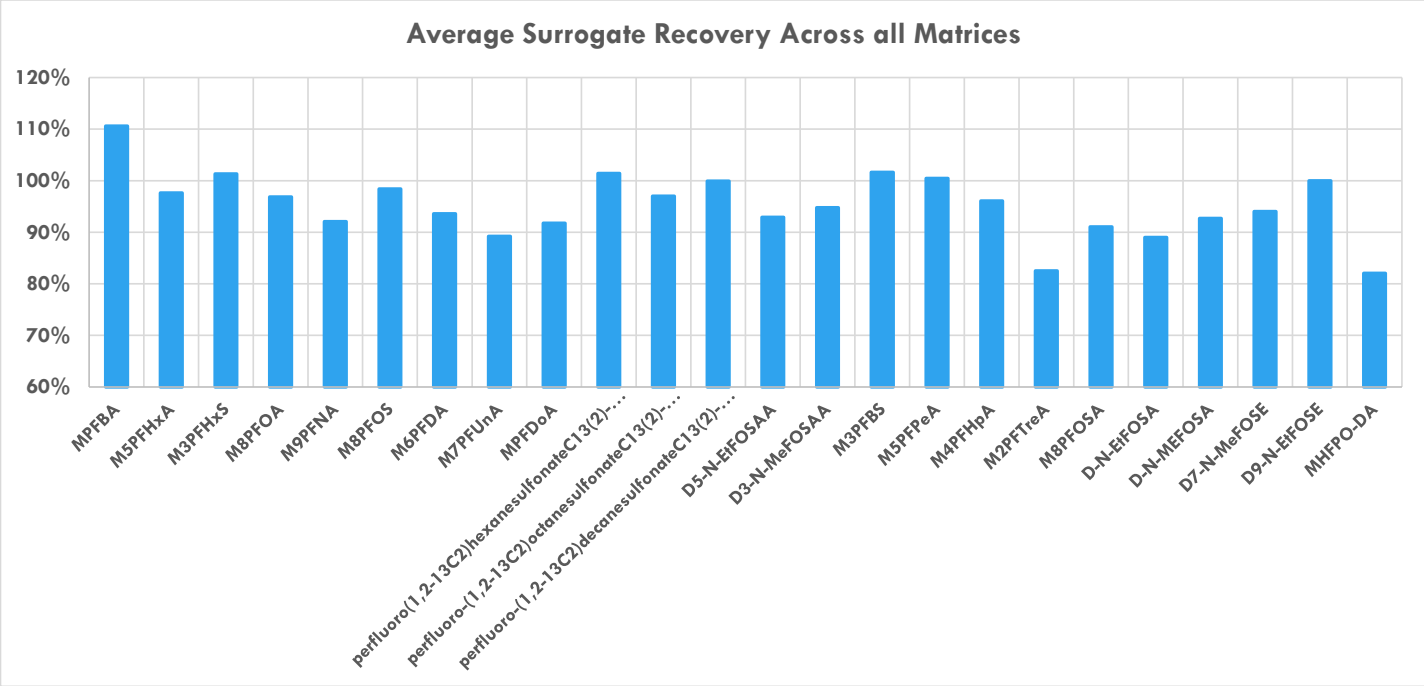
PULP AND PAPER MATRIX (160 NG/L)



PULP AND PAPER MATRIX (320 NG/L)



AVERAGE SURROGATE RECOVERY (160 NG/L SPIKE)



All surrogates between 82 – 111%

CONCLUSIONS

- ROBUST VALIDATED PFAS METHOD FOR 44 ANALYTES
- **THESE ARE ALL BY EXTERNAL CALIBRATION!** NONE OF THIS IS BY ISOTOPE DILUTION.
- THOROUGH SIMPLE SAMPLE PREPARATION
- 24 ISOTOPES USED TO **MONITOR** RECOVERY OF 44 TARGET ANALYTES
- AS MORE ISOTOPES BECOME AVAILABLE, THEY MAY BE ADDED
- FULL SET OF QC PER BATCH (MBs, MRLs, LCSs, DUPs, MSs). EVERY BATCH STANDS ON ITS OWN.
- THE ISOTOPES MAY BE USED FOR ISOTOPE DILUTION CORRECTION FOR THEIR NATIVE COUNTERPART ONLY. SURROGATE CORRECTION IS NOT ALLOWED.
- **"ISOTOPE DILUTION,** RADIOCHEMICAL METHOD OF ANALYSIS FOR MEASURING THE MASS AND QUANTITY OF AN ELEMENT IN A SUBSTANCE. THE PROCEDURE INVOLVES ADDING TO A SUBSTANCE A KNOWN QUANTITY OF A RADIOISOTOPE OF THE ELEMENT TO BE MEASURED AND MIXING IT WITH THE STABLE ISOTOPE OF THE ELEMENT." (REFERENCE- ENCYCLOPEDIA BRITANNICA)