Potomac Aquifer Recharge Monitoring Laboratory (PARML)

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Focus of This Presentation –

Method Development for Measurement of Selected PFAS Compounds in Water

Method Development and Validation

Ready to move combined USEPA Method 521 (Nitrosamines) and USEPA Method 522 (1,4 Dioxane) to comparison with other laboratories using traditional 521 and 522 methods separately.

(We have reported on this method's development and preliminary results at previous PAROC meetings)

PARML Development of a PFAS Perfluorocarboxylic Acid (PFC) Analytical Method

Possible Screening Level Tool

Requirements for an Alternate PFAS Analytical Method

- Must be substantially robust/stable
- Must have detection limits comparable to approved EPA methods
- The method should follow well established analytical procedures and minutely detailed (described)
- The method should be published in the refereed literature

Current Analytical Methods for PFAS Compounds in Water

EPA METHOD 533:

DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER BY ISOTOPE DILUTION ANION EXCHANGE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY

EPA METHOD 537.1:

DETERMINATION OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Attributes and Characteristics of Current EPA Methods

Both are established analytical procedures developed, approved, and published by EPA and used at numerous laboratories

Require larger volumes of sample where analytes are concentrated through solid phase extraction (SPE) then elution before injection onto a LC MS/MS

The procedures are analyst time intensive, SPE step is often the bottleneck, LC/MS/MS run times of 25-35 minutes per sample have been reported, and overall turn around times can be lengthy. (Long turnaround times currently reported due to large quantity of samples being handled by commercial laboratories)

PARML Efforts to Develop an Alternate PFAS Analytical Method

Uses a triple-quadrupole GC/MS in MRM with internal standard and surrogate compound

No solid-phase extraction required

Derivitization of polyfluorocarboxylic acids into volatile forms in 50 mL sample with preparation and reaction of 5 minutes at room temperature. Stripped and separated by GC and identified by tandem MS.

Can measure haloacetic acids (HAAs) in the same run

PARML Efforts to Develop an Alternate PFAS Analytical Method (cont.)

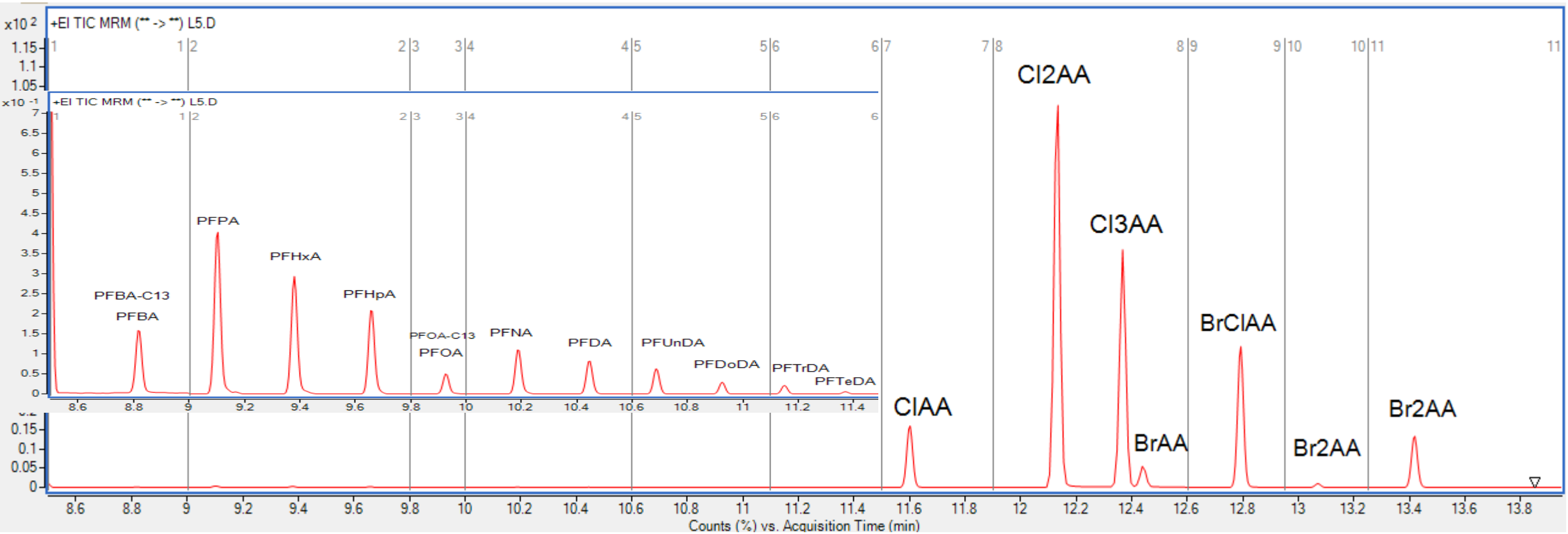
Sample run time of 14 minutes. Same day sampling and results

Method still in development and results considered preliminary

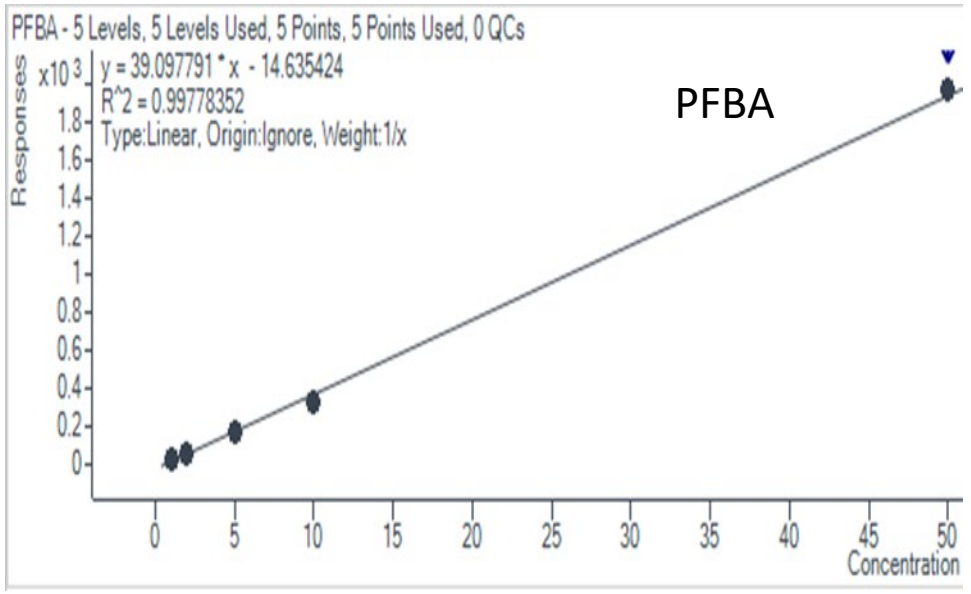
Perfluorocarboxylic Acids Determined in PARML Triple Quad GC/MS Method

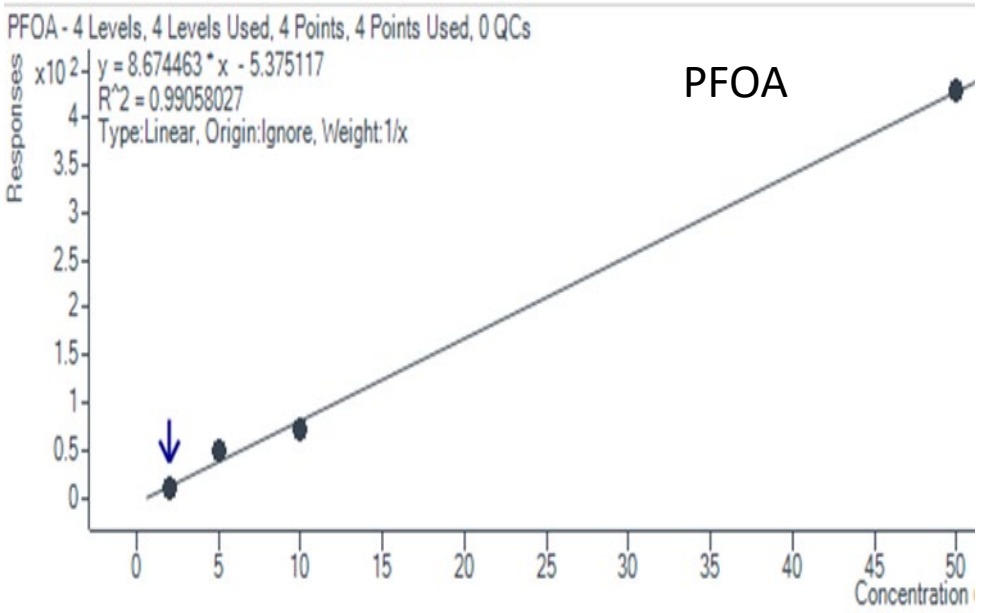
Abbrev.	Common Name	# Carbons	chain length
PFBA	Perfluorobutanoic acid	4	short
PFPA	Perfluoropentanoic acid	5	short
PFHxA	Perfluorohexanoic acid	6	short
PFHpA	Perfluoroheptanoic acid	7	long
PFOA	Perfluorooctanoic acid	8	long
PFNA	Perfluorononanoic acid	9	long
PFDA	Perfluorodecanoic acid	10	long
PFUnA	Perfluoroundecanoic acid	11	long
PFDoA	Perfluorododecanoic acid	12	long
PFTrA	Perfluorotridecanoic acid	13	long
PFTeA	Perfluorotetradecanoic acid	14	long

PARML-Developed Method For PFCs and HAAs
Detection limit 2 ng/L (PFOA, PFBA)
HAAs= 0.1 ug/L



Standard Curves

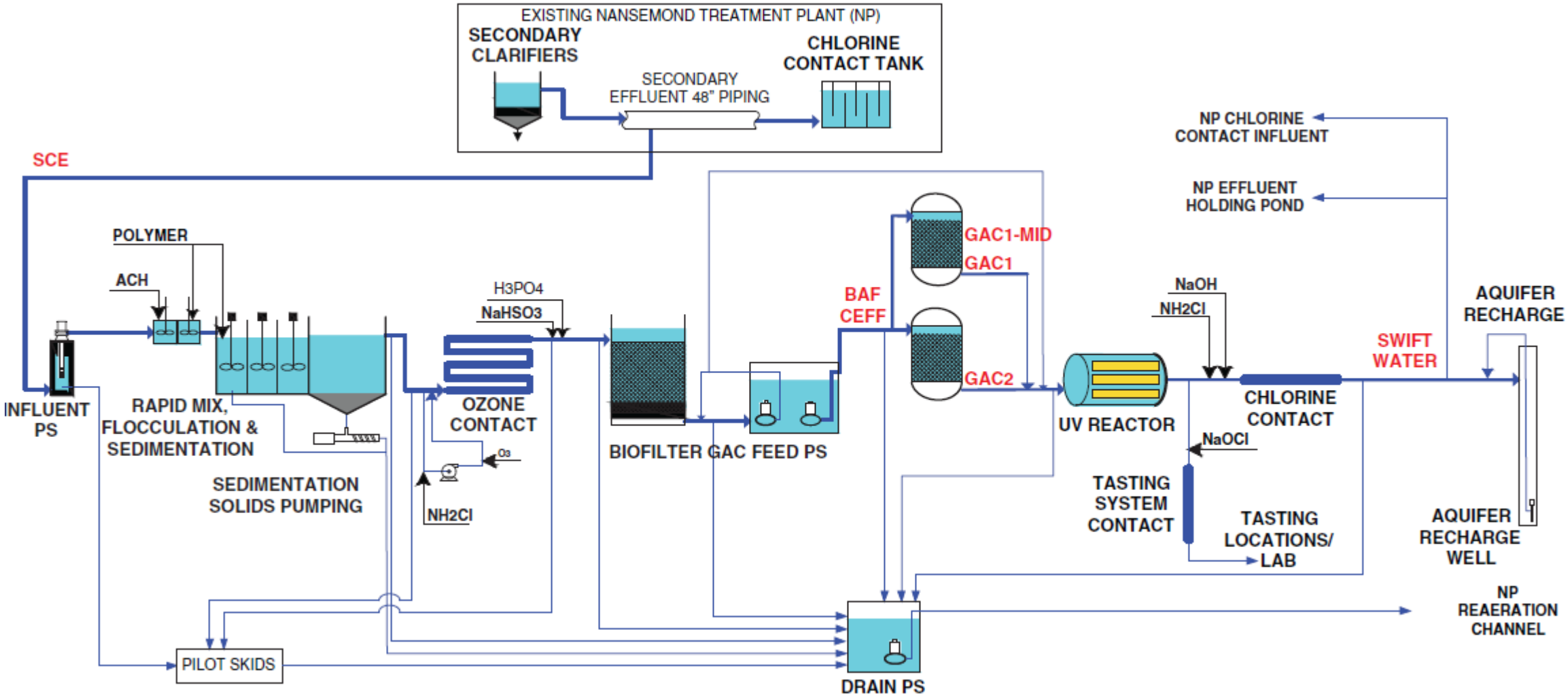




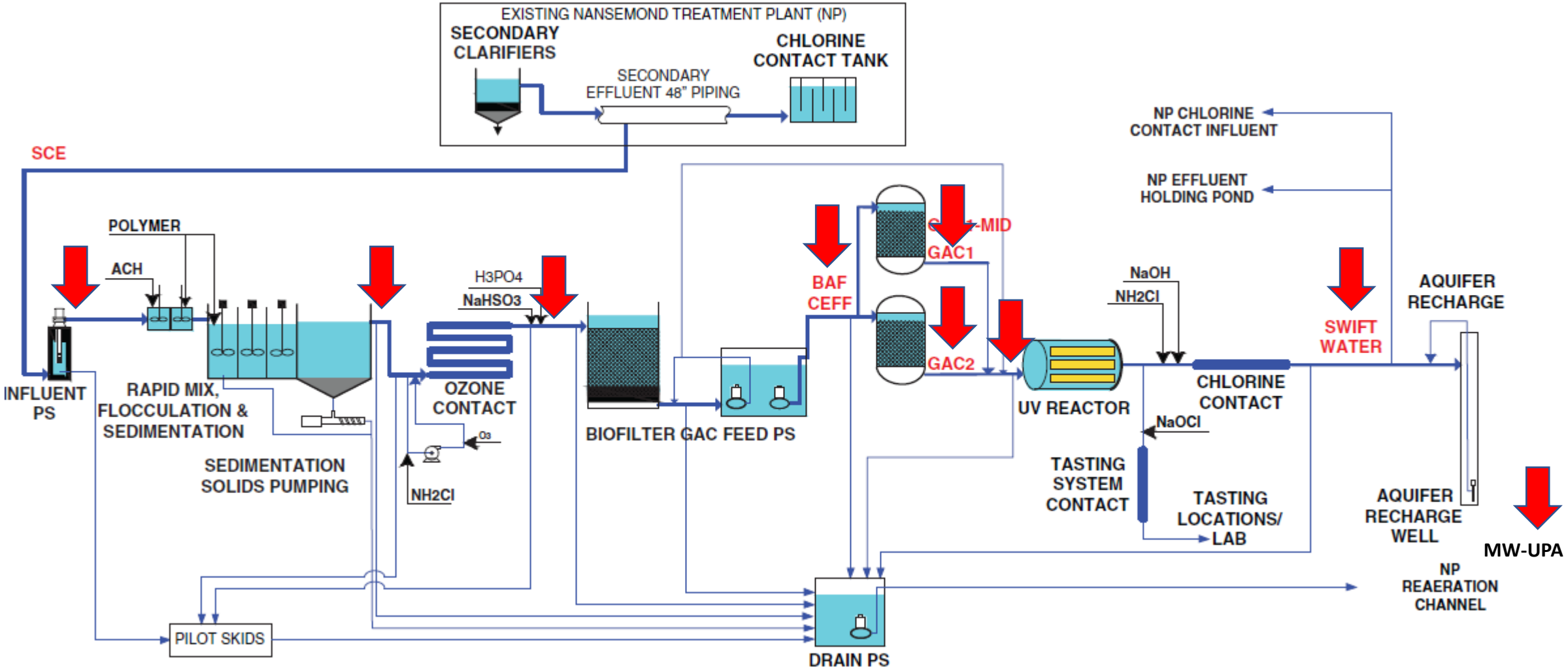
Have Begun Effort to Compare PARML Results with Commercial Laboratory From Samples Collected at SWIFT RC

First Date: Tuesday November 29, 2022

Process Schematic for SWIFT Research Center



Sampling Points for Analytical Comparisons



Perfluorocarboxylic Acid Concentrations at Sampling Points Across the SWIFT RC Treatment Process Train (11/29/2022)

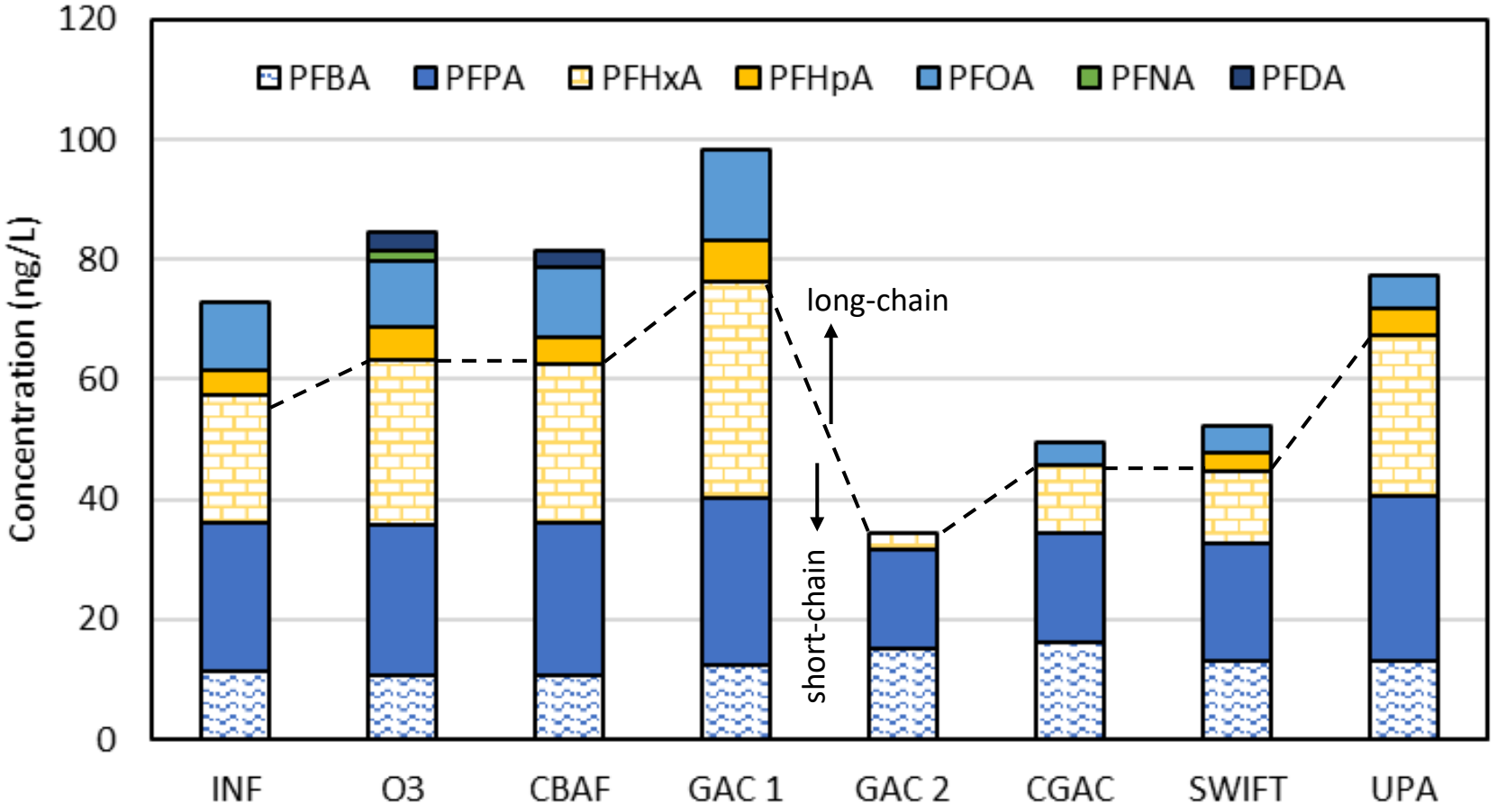
Compound	INF (ng/L)	O_3 (ng/L)	CBAF (ng/L)	GAC 1 (ng/L)	GAC 2 (ng/L)	CGAC (ng/L)	SWIFT (ng/L)	UPA (ng/L)	QC (10 ng/L)	MQ (ng/L)
PFBA	11.3	10.6	10.6	12.5	15.2	16.1	13.2	13.1	9.53	0?
PFPA	24.9	25.1	25.4	27.8	16.5	18.2	19.5	27.6	9.3	0
PFHxA	21.1	27.5	26.5	36.1	2.5	11.3	12.1	26.5	10	0
PFHpA	4.3	5.44	4.43	6.74	0	0	2.81	4.51	10.5	0
PFOA	11.1	11	11.9	15.2	0	4.02	4.7	5.77	11.2	0
PFNA	0	1.88	0	0	0	0	0	0	10.2	0
PFDA	0	3.12	2.47	0	0	0	0	0	11.2	0
PFUnA	0	0	0	0	0	0	0	0	8.75	0
PFDoA	-	-	-	-	-	-	-	-	-	-
PFTrA	0	0	0	0	0	0	0	0	13.71	0
PFTeA	0	0	0	0	0	0	0	0	11.05	0

MQ is deionized laboratory water

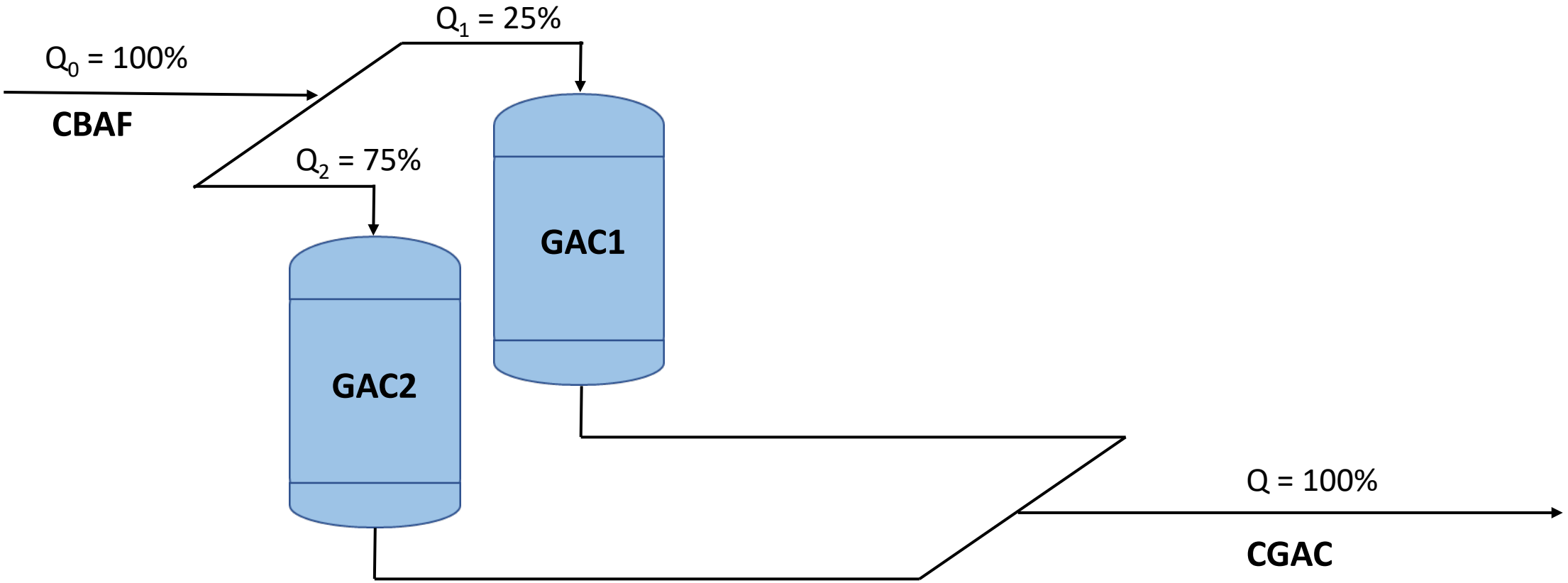
QC is measured results of MQ water made up to 10 ng/L and run as a sample

Considered preliminary results while method is still in development; duplicate sample not spiked or surrogate used for this run.

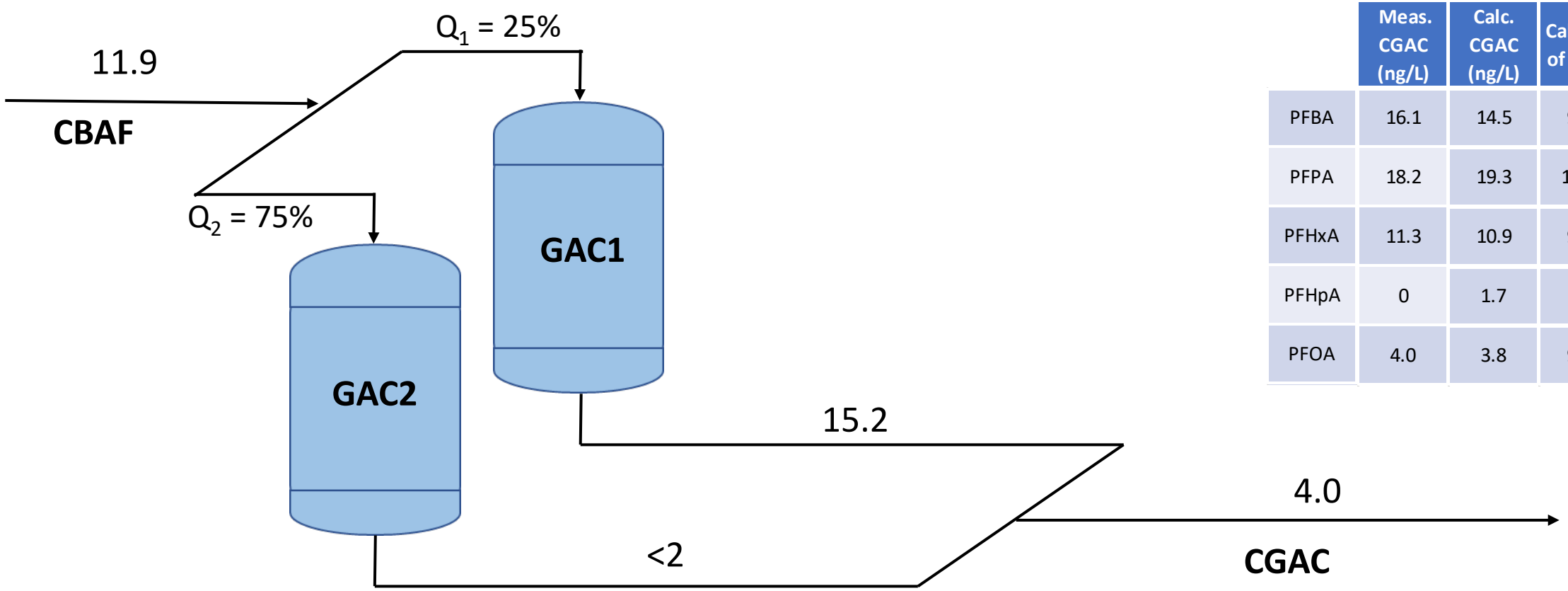
Perfluorocarboxylic Acid Concentrations at Sampling Points Across the SWIFT RC Treatment Process Train



Current Flow Split Across GAC Columns at SWIFT Research Center



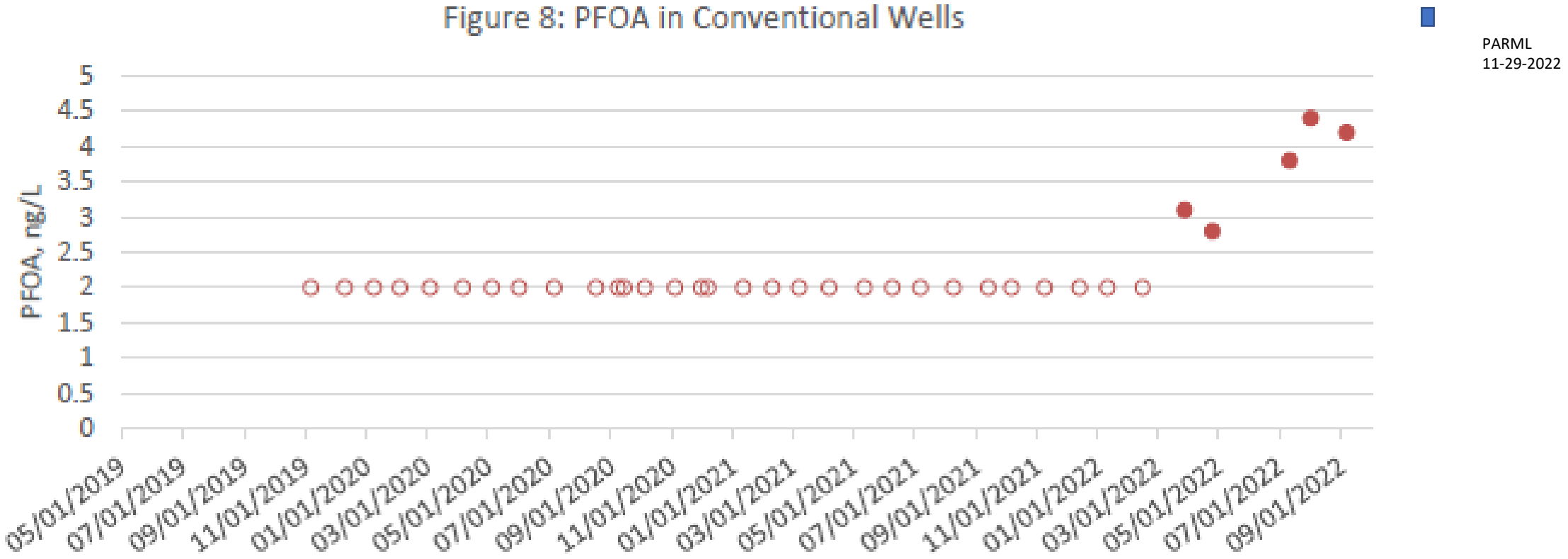
Measured PFOA Concentrations Across GAC Columns at SWIFT Research Center



	Meas. CGAC (ng/L)	Calc. CGAC (ng/L)	Calc as % of Meas.
PFBA	16.1	14.5	90%
PFPA	18.2	19.3	106%
PFHxA	11.3	10.9	96%
PFHpA	0	1.7	
PFOA	4.0	3.8	95%

(by mass balance calculation = 3.8)

PFOA Measurements in MW-UPA Well at SWIFT Research Center



HRSD SWIFT Research Center 2022 3rd Quarterly Report (red circles)

Notes:

PARML PFAS method still being evaluated, and data values should still be considered preliminary (not to be cited/reported)

We learned in a second round of sampling where sodium thiosulfate was added to quench chlorine (so that HAAs could be measured), that the thiosulfate interfered with the analyses

Haloacetic Acids Analysis of SWIFT Water

Compound (SWIFT)	PARML (10/20/22) (ug/L)	QR (09/06/22) (ug/L)
ClAA	2.5	<0.6
Cl_2AA	2.0	2.1
Cl_3AA	0.9	0.5
BrAA	Y	0.72
Br_2AA	10.7	6.4
BrClAA	5.4	-

Preliminary Results

Developing other Analytical Capabilities

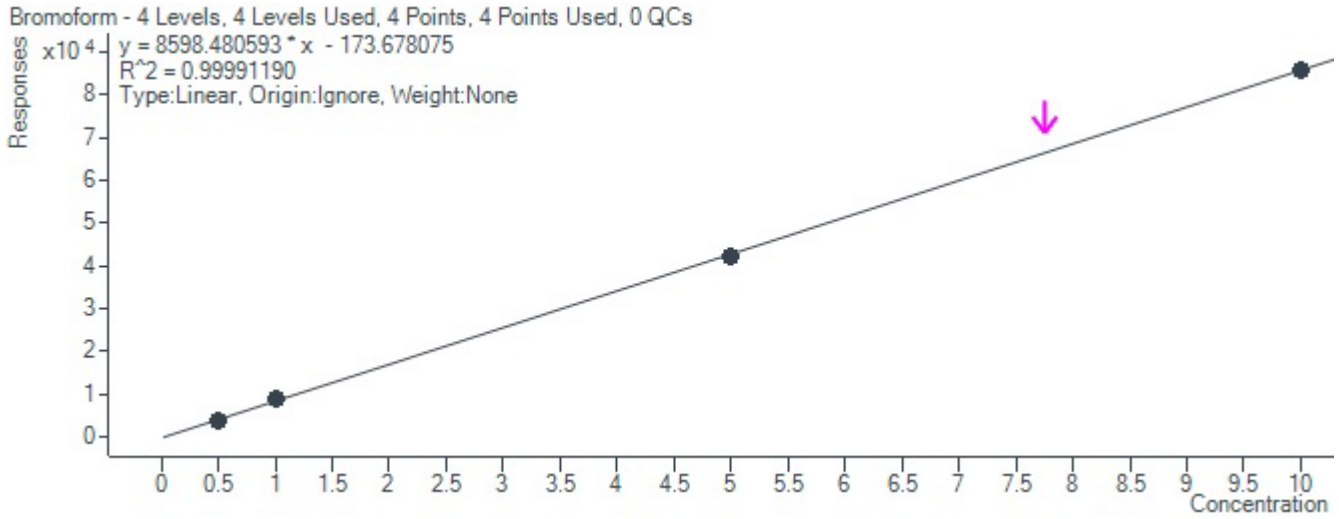
Acquired ITEX unit for GC autosampler that allows automated purge and trap analyses for volatile organic compounds (EPA 502-524)

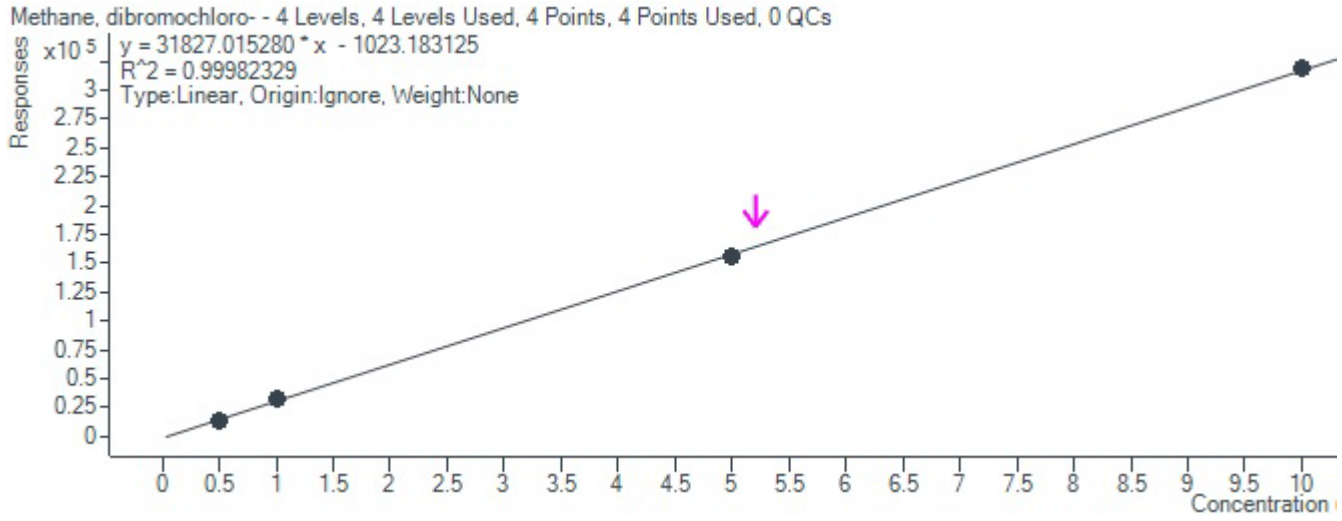
First class of compounds examined - halomethanes

VOCs (THM)
(EPA 502, ITEX)

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon Tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-Chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropylbenzene	99-87-6
Methylene Chloride	75-09-2
Naphthalene	91-20-3
Propylbenzene	103-65-1
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	630-20-6
1,1,1,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluormethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl Chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

Calibration curves for Bromoform and Dibromochloromethane





Comparison of SWIFT THM Values Reported from Sept 2022 (SWIFT program quarterly report) and PARML measurement in November

Halomethanes in SWIFT Water

Compound/Sample	SWIFT (Sep 2022) Quarterly Report (ug/L)	SWIFT (Nov 2022; PARML) (ug/L)
Bromochloromethane ($BrClM$)	NR	0.03
Bromodichloromethane ($BrCl_2M$)	2.58	1.35
Bromoform (Br_3M)	7.85	7.75
Chloroform (Cl_3M)	<1.00	0.67
Dibromochloromethane (Br_2ClM)	7.49	5.20
Dibromomethane (Br_2M)	NR	0.02
Iodomethane (IM)	NR	0

Trihalomethanes

Method Development in Process

Measurement of PFOS and other sulfur-containing PFAS molecules

Acknowledgement

Dr. Seyyedhadi Khatami - method development efforts at PARML

Questions