Subsampling Heterogeneity of High Surfactant Activity Aqueous Samples: Implications for Perfluorinated Compound Analysis

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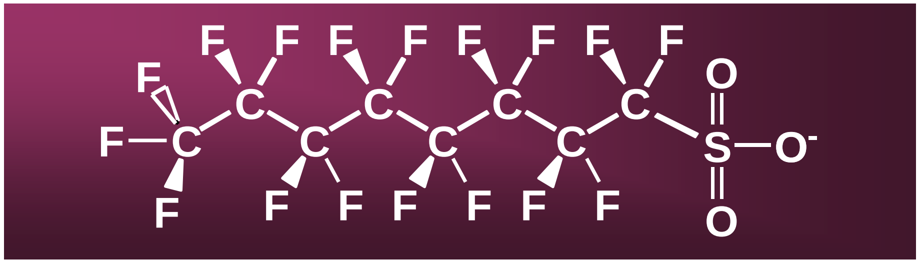
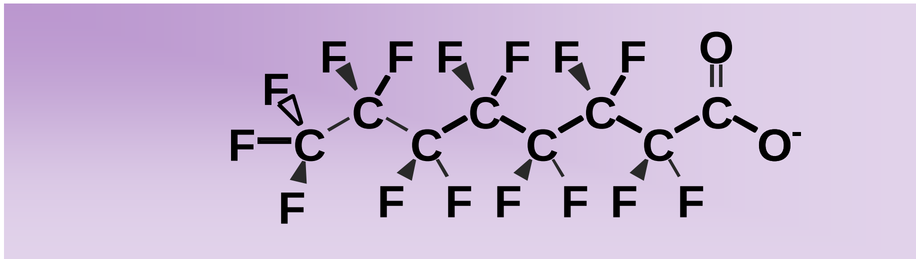
Perfluorinated Surfactants

- Perfluorinated Sulfonates: e.g. PFOS (C4, C6 and C8)



- Perfluorinated Carboxylates: e.g. PFOA (C4-C12)



Industrial and Consumer Uses

- Fabric coatings
- Carpet coatings
- Paper coatings
- Floor polish
- Alkaline cleaners
- Denture cleaners
- Shampoos
- Ant/roach insecticides
- Fire-fighting foam
- Aviation hydraulic fluid
- Mining/oil well surfactant
- Acid rust suppressant
- Metal plating
- Electronic etching bath

Select Applications

- Chrome Plating
  - Fume suppression: Example: Fumetrol 140: PFS : 1-7% by wt. Use 0.25% of bath by volume
  - Also used in plating process as an etching agent to increase coating effectiveness

AFFF Foams

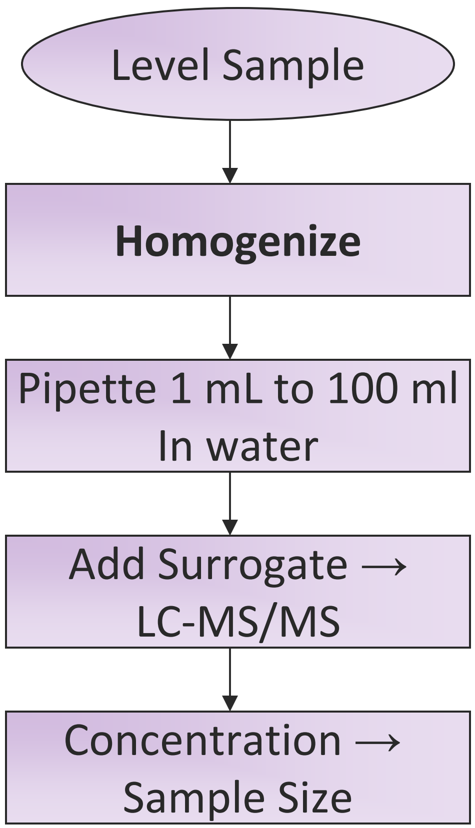
- Aqueous Film Forming foams used in fire suppression sometimes contain PFOS – Sites with years of use, e.g. military and airports affected.
- Also contain non fluorinated hydrocarbon surfactants that enhance surfactant activity
- 0.5-1.5% w/w PFOS/other sulfonates. Now being replaced by perfluorocarboxylate fluorotelomer products

Typical AFFF Formulation (FC-203CF)

Component	Composition (%)
Water	69.0–71.0
Diethyleneglycolbutylether (Butyl Carbitol)	20
Amphoteric fluoroalkylamide derivative	1–5
Alkyl sulfate salts	1.0–5.0
Perfluoroalkylsulfonate salts	0.5–1.5
Triethanolamine	0.5–1.5
Tolyltriazole (Corrosion inhibitor)	0.05

- Both hydrocarbon and fluorocarbon surfactants
- Organic solvent
- Stable film and foam formation

Prescreening Protocol



- Useful where variety of samples present
- Reduces instrument carryover, rework due to calibration range overshoots
- Optimizes detection limits for low level samples in work containing high level samples

Result Reproducibility

AFFF Site

Analyte	Original (ng/L) 0.25 L	Repeat (ng/L) 0.01 L
PFBA	2,800	2,750
PFHXA	11,600	9,120
PFOA	2,590	3,510
PFBS	3,320	1,190
PFHXS	13,000	3,840
PFOS	22,000	4,000

Chrome Plating Site

Analyte	Original (ng/L) 0.25 L	Repeat (ng/L) 0.01 L
PFBA	23.3	ND 125
PFHXA	55.4	ND 125
PFOA	ND 4.92	ND 125
PFBS	>20000	2,670
PFHXS	ND 9.84	ND 250
PFOS	19,600	ND 250

In both cases, pre-screen indicated low level sample

Observational Results

- Differences between pre-screening, original and repeat results
  - Seen in effluent stream and roof top snow melt
- Seen multiple times in samples from high level sites/samples with surfactant activity
- Samples showing foam formation on homogenization associated with discrepancies
  - Not all samples showing foam formation show this effect
  - Samples that did not foam sometimes showed effects

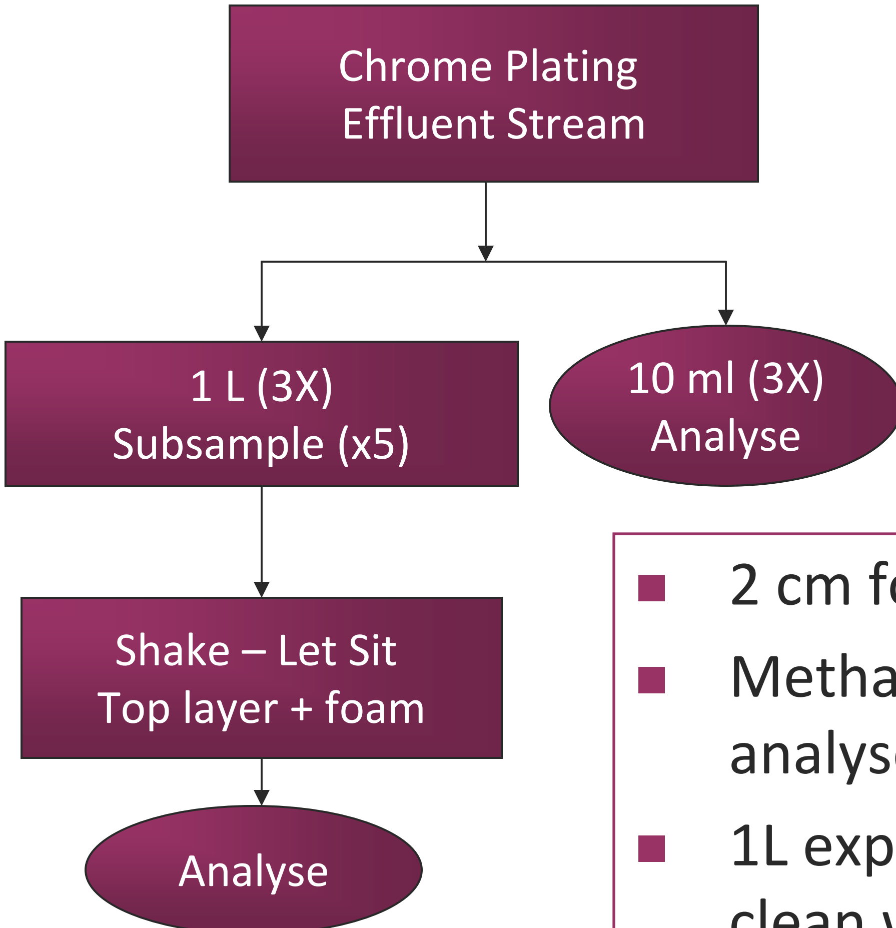
Experiment Objectives

- Reproducibility of subsampling under controlled conditions
- Comparison of large and small sample sizes
  - Can a smaller sample accurately represent a 1 L sample
- Exploration of other sampling protocols
  - No homogenization
  - Stirring

Sample Details

- Effluent samples used for this experiment grab sampled directly from flowing stream from chrome plating facility
  - 8 each of 1 L and 10 mL samples collected by MPCA
  - Study 1 used "fresh" samples (3 each)
  - Study 2 used samples that had been frozen 3+ months (five remaining 1 L samples)

Subsampling Experiment (Study 1)



- 2 cm foam layer seen
- Methanol rinses analysed (just in case)
- 1L experiment with clean water as well

Analysis Protocol

Adjust pH to 6.5 ±0.5
Spike labeled surrogates

↓

SPE extraction with WAX
Condition: 5 mL 0.3% NH4OH in MeOH and 5mL0.1 M HCOOH

↓

Wash: with 5 mL of H_2O 5 mL &
With 1:1 (0.1 M HCOOH: MeOH)

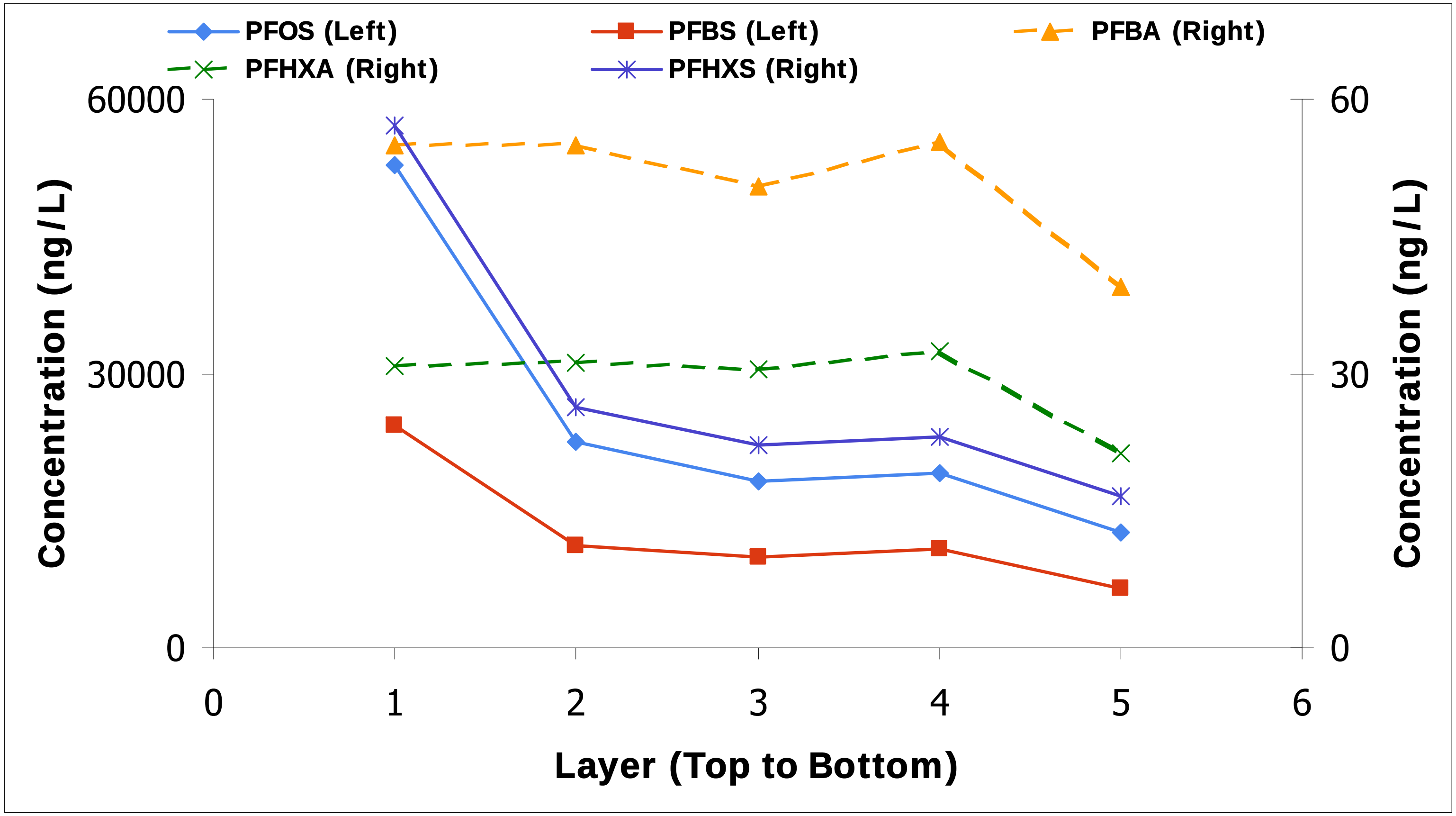
↓

Elute: 4 mL of 0.3% NH4OH in MeoH
Microvial 300uL portion

↓

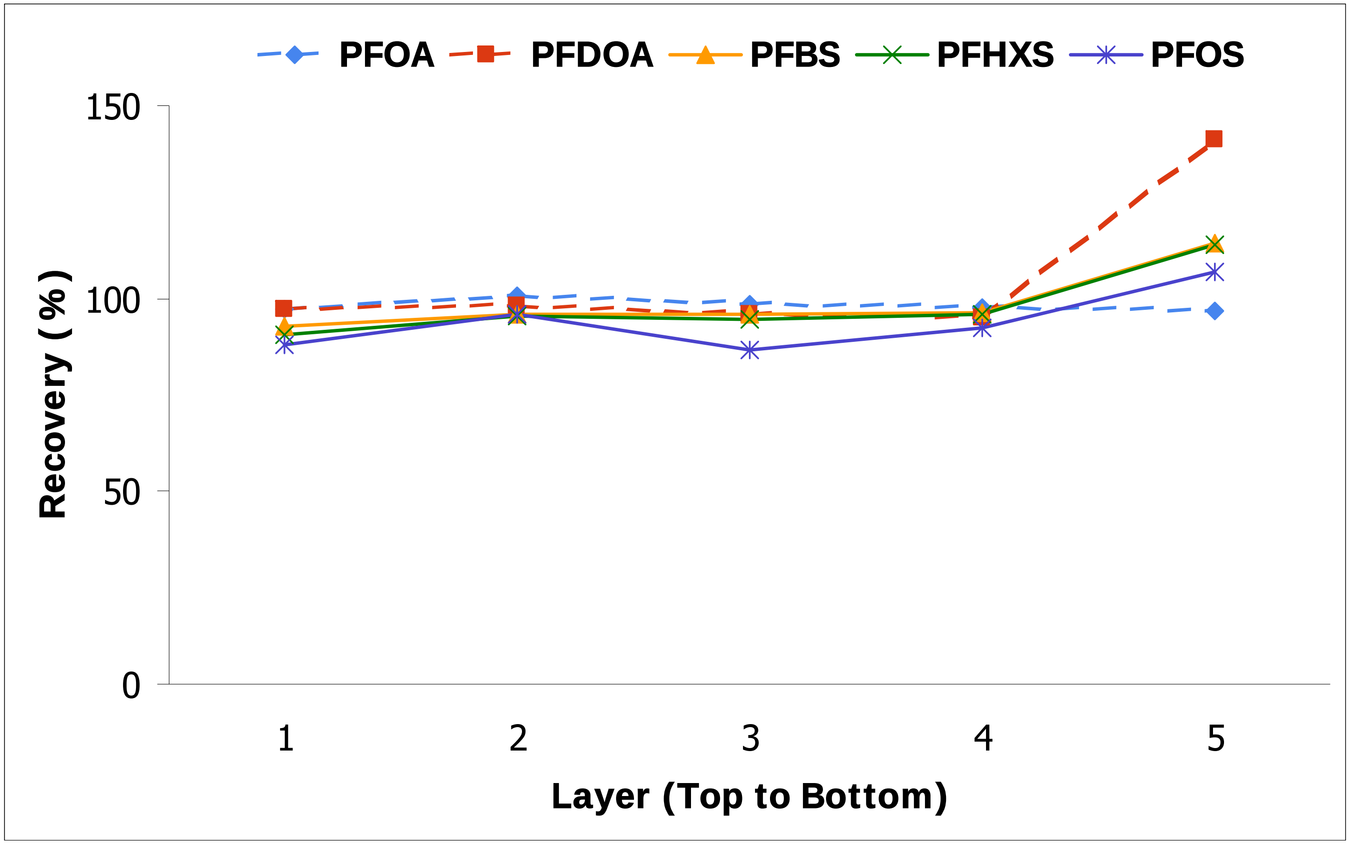
Analyze by (-ESI) LC-MS/MS

Stratification Results – 1L Effluent



PFOS – Difference between Layer 1 and 2 significant at $p = 0.002$

Results – Spiked Clean Water



Mass Balance 1 L samples vs. 10 mL

Analyte	1 L Total (ng)	10 mL Extrapolated (ng)
PFBA	51.3	64.8
PFHxA	29.2	21.8
PFBS	12600	8160
PFHxS	29.1	ND
PFOS	25400	30700

- Reasonable agreement between small and large sample – Field subsampling worked

Significant Findings – Shaking Study 1

- Reproducible stratification of PFS analytes
- No such stratification of PFCA analytes
- Stratification seen even for low concentration PFS analytes in the presence of higher concentration of other PFS
- Clean water sample with similar spiked levels of PFCA and PFS does not show same behaviour – Non-analyte surfactants?

No Shaking? Stirring? Study 2

Sample	Treatment	Layers (200 mL each)	Replicates
Control	Shake and Sit	3 (Top, middle, bottom)	1
Static	None	3 (Top, middle bottom)	2
Dynamic	Continuous magnetic stirring	3 (Moving sample)	2

Experiment carried out 3 months later

Study 2 Results

	Shaken Totals (ng/L)	Static Totals (ng/L)	Stirred Totals (ng/L)	Shaken Totals (Exp1 ng/L)
Stratification?	None	None	None	P=0.002
PFBA	52.1	53.3	51.3	51.3
PFHxA	38.8	42.2	35.5	29.2
PFBS	11400	11900	14300	12600
PFHxS	21.2	18.7	21.1	29.1
PFOS	21500	28800	27400	25400

- Stratification not seen in this experiment
  - Samples had been stored (frozen) 3 months?
- Stirred data very close to totals in first experiment and 10 mL results
- Experiment inconclusive

Conclusions

- Avoid lab subsampling if at all possible – Good sampling design and appropriate sample size
  - Provide two separate samples 1 L and 10 mL, for example
  - Duplicates and MS/MSDs help identify the effect
- Shaking samples to homogenize results in the formation of a foamy layer that can stratify PFS analytes
  - Other surfactants present in samples maybe involved
- Stirring of samples creates no foam while moving entire column, promising
  - Further work ongoing in the laboratory
- In the field, harder to control – Watch and control for surfactant activity – Foam. Know your sources

Questions?