



Update from ECL:

New and Ongoing Work on PFASs

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**Biomonitoring California Scientific Guidance Panel
August 22, 2018, Oakland, CA**

Outline

- Overview of current PFASs methods
- Limited biomonitoring study of three firefighters accidentally exposed to firefighting foam
- Current/upcoming work in ECL

Targeted PFASs Methods

Classic



+ FA + Labeled IS



Automated Online SPE /
LC-MS/MS



12 PFAS

Targeted PFASs Methods

Classic



+ FA + Labeled IS



Automated Online SPE /
LC-MS/MS



12 PFAS

Compounds Measured

PFHpA

PFOA

PFNA

PFDA

PFUdA

PFDoA

PFBS

PFHxS

PFOS

PFOSA

MeFOSAA

EtFOSAA

Targeted PFASs Methods

Expanded



+ Labeled IS

Liquid-Liquid Extraction

Envicarb Clean-Up and
Evaporation

LC-MS/MS

~30 PFAS

Classic and Expanded PFASs List

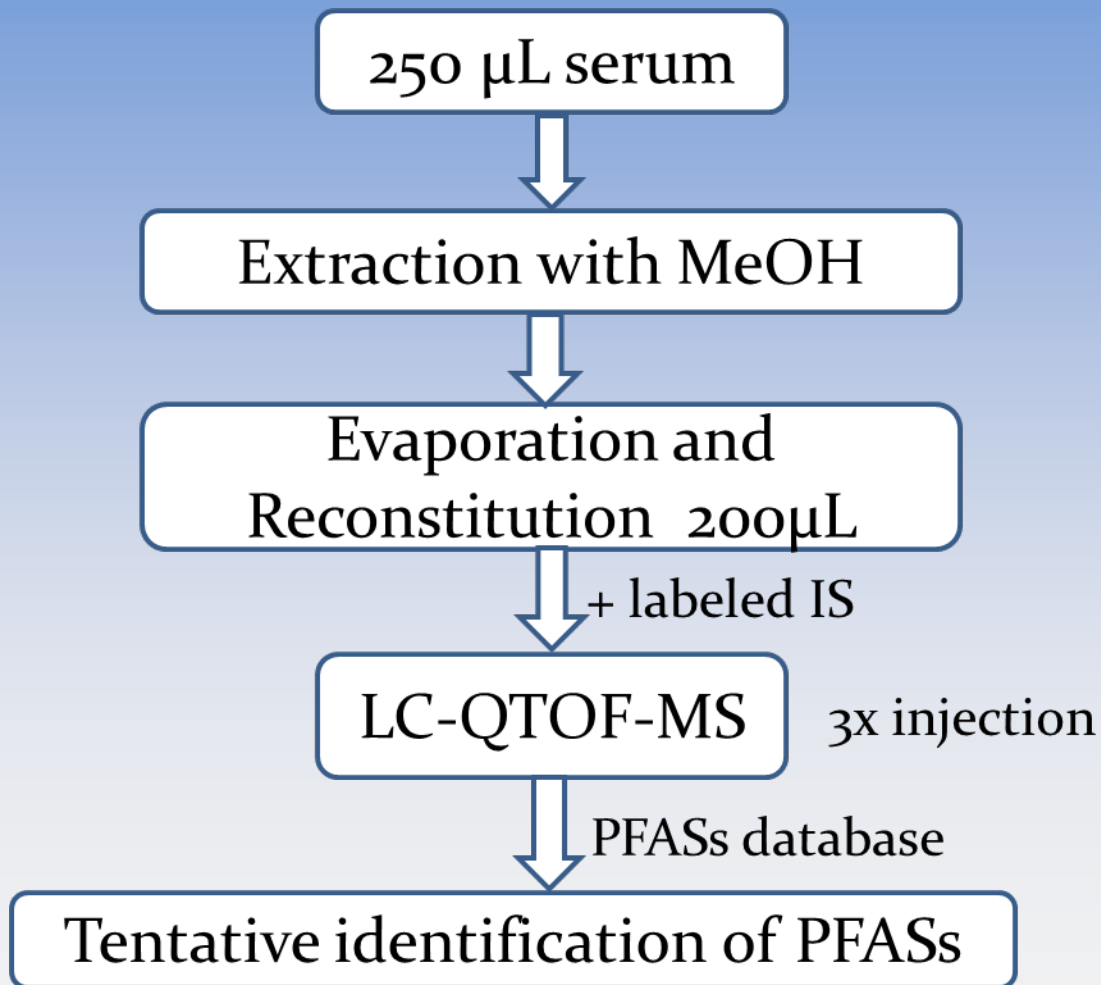
Classic
PFHpA
PFOA
PFNA
PFDA
PFUdA
PFDoA
PFBS
PFHxS
PFOS
PFOSA
MeFOSAA
EtFOSAA



Additional Classic
PFBA
PFPeA
PFHxA
PFDS

Replacement/Precursors
FPePA/5:3 FTCA
FHpPA/7:3 FTCA
FHEA/6:2 FTCA
FOEA/8:2 FTCA
FHUEA/6:2 FTUCA
FOUEA/8:2 FTUCA
4:2 FTS
6:2 FTS
8:2 FTS
8:2 PAP
6:2 diPAP
8:2 diPAP
6:6 PFPi
6:8 PFPi
PFHxPA
PFOPA

Semi-Targeted Method



Limited Study - Background

- What we know:
 - Physician requested analysis of PFASs in serum samples from three male firefighters
 - Individuals were accidentally exposed to firefighting foam



Limited Study - Background

- What we know:
 - Physician requested PFASs analysis on serum samples from three male firefighters
 - Individuals were accidentally exposed to firefighting foam
- What we don't know:
 - Specifics of accidental exposure
 - Type of foam to which they were exposed
 - Time between exposure and collection
 - Information on other possible PFASs exposure



Results from Classic Method

	MDL	Firefighter A	Firefighter B	Firefighter C
PFOSA	0.05	0.08	<MDL	<MDL
MeFOSAA	0.01	0.13	0.07	0.13
PFHxS	0.02	7.5	4.6	10.1
PFOS	0.20	26.2	5.7	30.8
PFHpA	0.05	<MDL	0.09	<MDL
PFOA	0.06	2.5	3.1	1.8
PFNA	0.05	1.1	0.78	0.23
PFDA	0.08	0.13	<MDL	<MDL
PFUdA	0.02	0.15	0.05	0.02

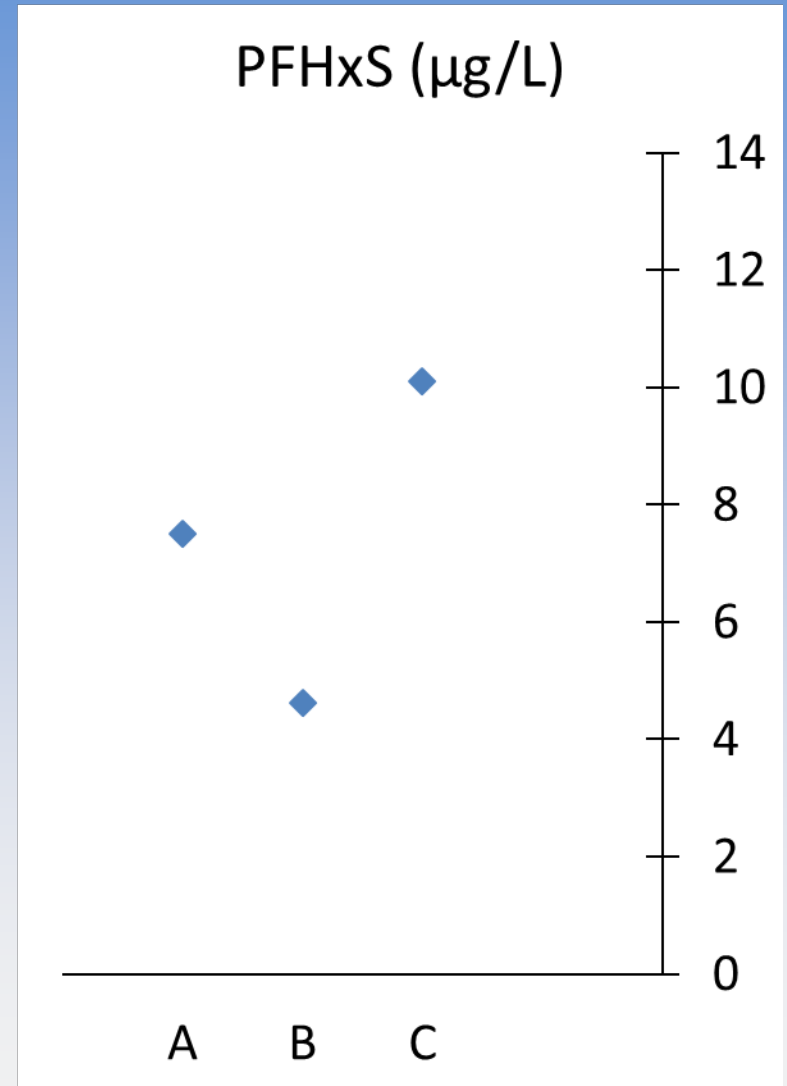
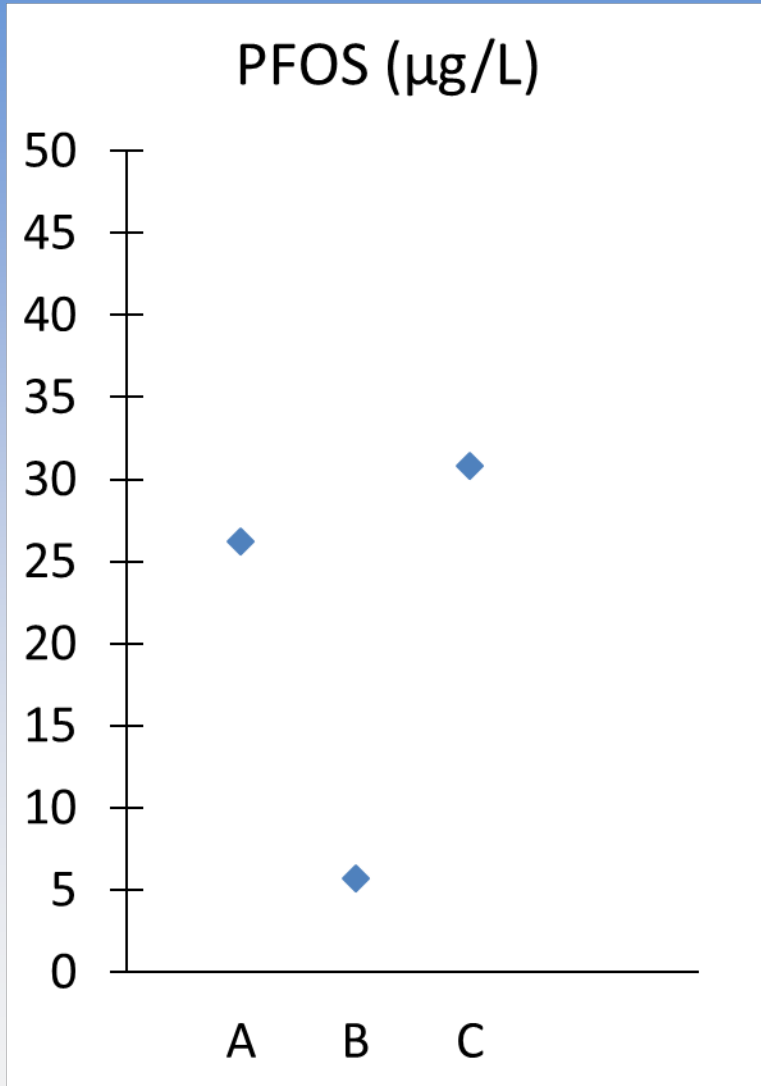
Units: $\mu\text{g}/\text{L}$

Results from Classic Method

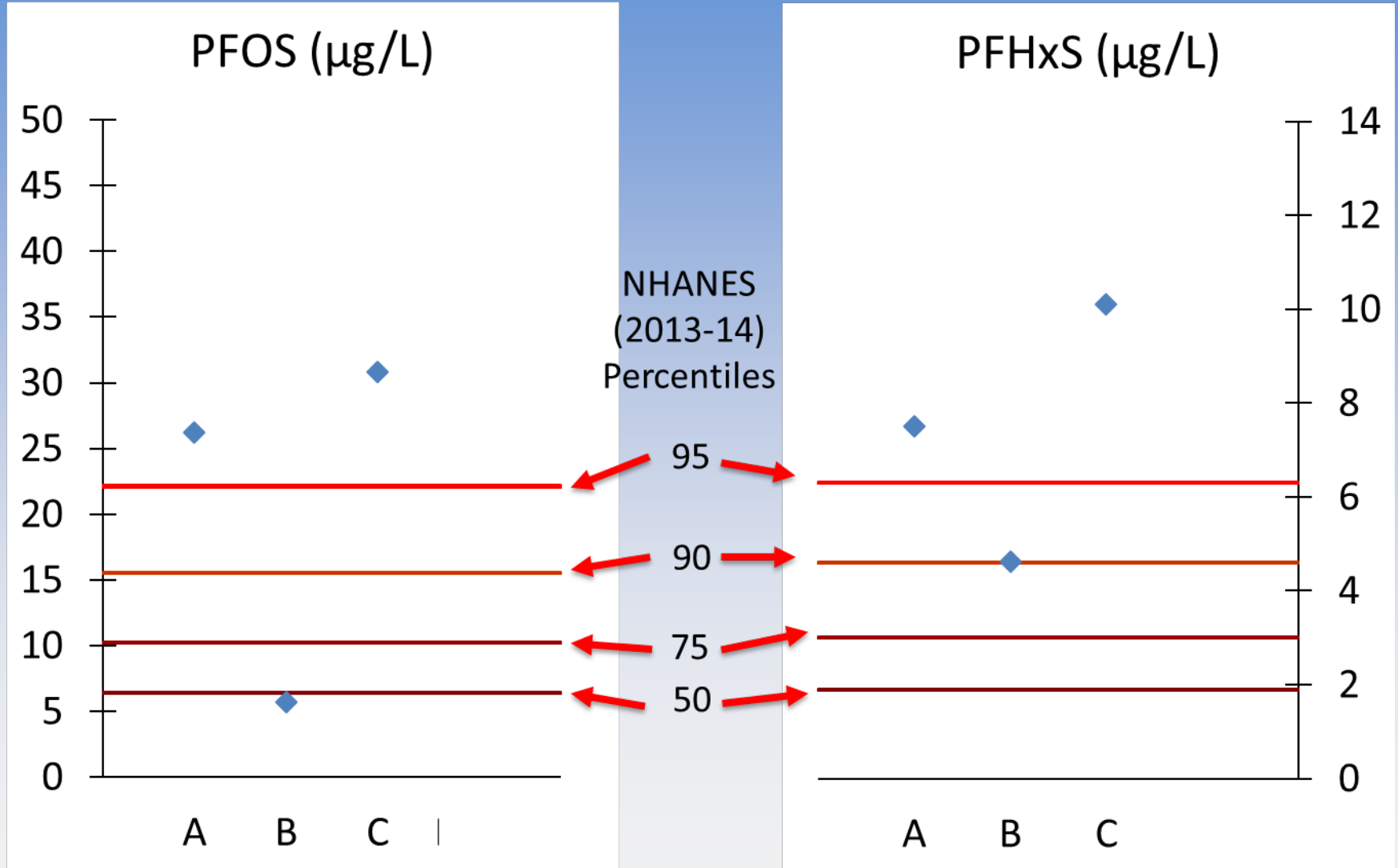
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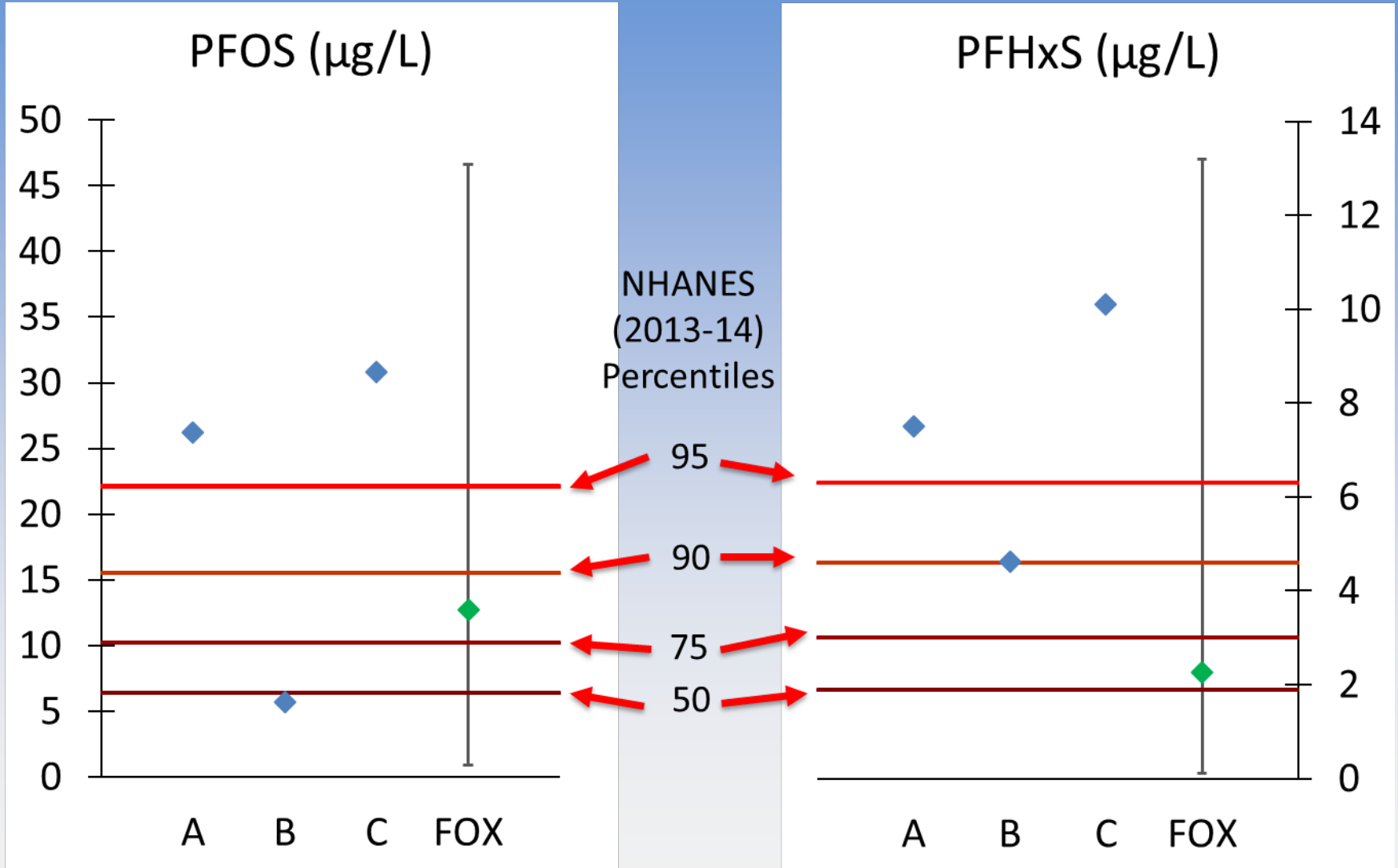
Comparison to Other Studies



Comparison to Other Studies



Comparison to Other Studies



Firefighting Foam Exposures

- AFFF (aqueous film-forming foam)
 - Proprietary mixtures that are used to extinguish fuel-based fires
 - Contain fluorinated surfactants to aid in fire suppression
- Manufacturing process leads to different degradation products
 - Could be used to “fingerprint” the type of AFFF exposure

Firefighter PFAS Levels

- Factors affecting PFASs:
 - Male or female
 - Years on the job
 - Type of AFFF exposure
 - # of Blood donations

Results from Expanded Method

	MDL	Firefighter A	Firefighter B	Firefighter C
PFDS	0.01	0.01	<MDL	MDL
6:2 FtS	0.02	0.05	0.13	0.03
8:2 FtS	0.01	0.08	<MDL	0.03
6:2 diPAP	0.05	0.08	0.07	0.09

Units: $\mu\text{g/L}$

Results from Expanded Method

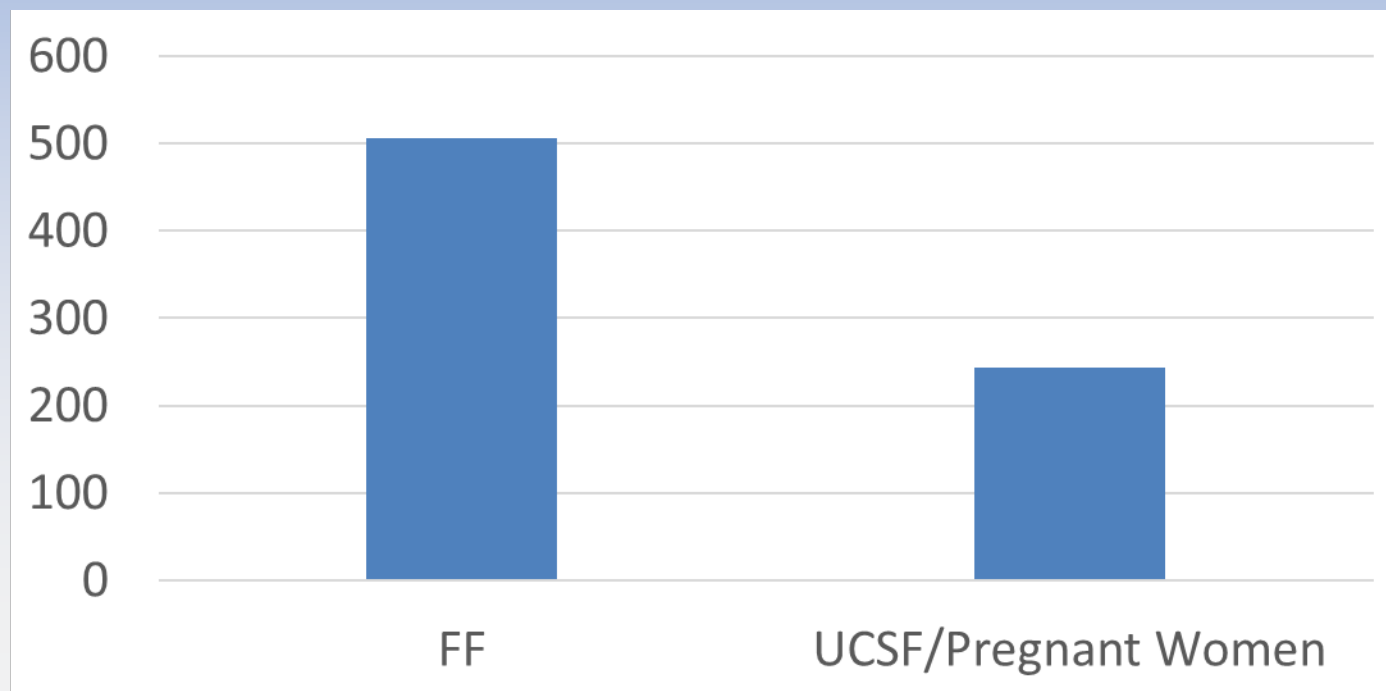
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6:2 FtS	0.02	0.05	0.13	0.03
8:2 FtS	0.01	0.08	<MDL	0.03
6:2 diPAP	0.05	0.08	0.07	0.09

Units: $\mu\text{g/L}$

Levels were similar to those found in
ACE 1 and ACE 2

Initial Results from Semi-Targeted Analysis

- In initial analysis over 3369 features (potential chemicals) were extracted
 - ~ 15% were F-containing features (506)



Screening/Library Search Results

- PFASs in the targeted analysis list found
- No additional firefighting foam compounds or environmental breakdown products found in the serum samples via the library search

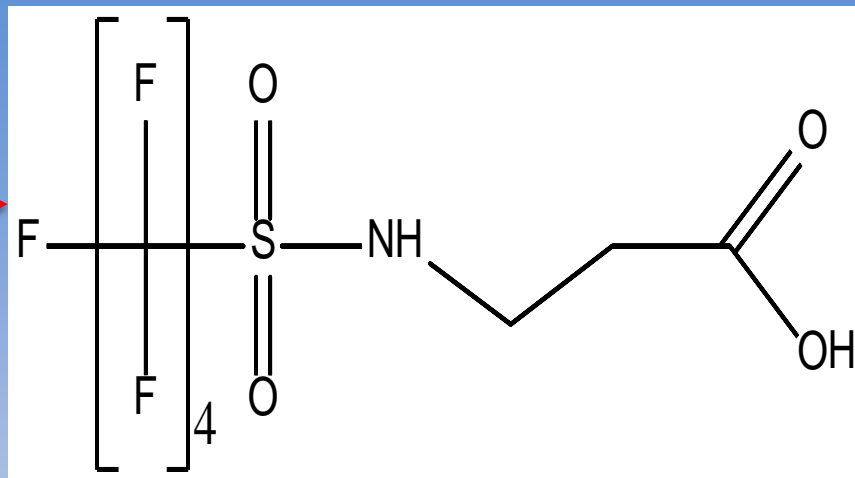
Screening/Library Search Results

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Were the compounds the firefighters were exposed to non-persistent in humans or metabolized into different compounds?

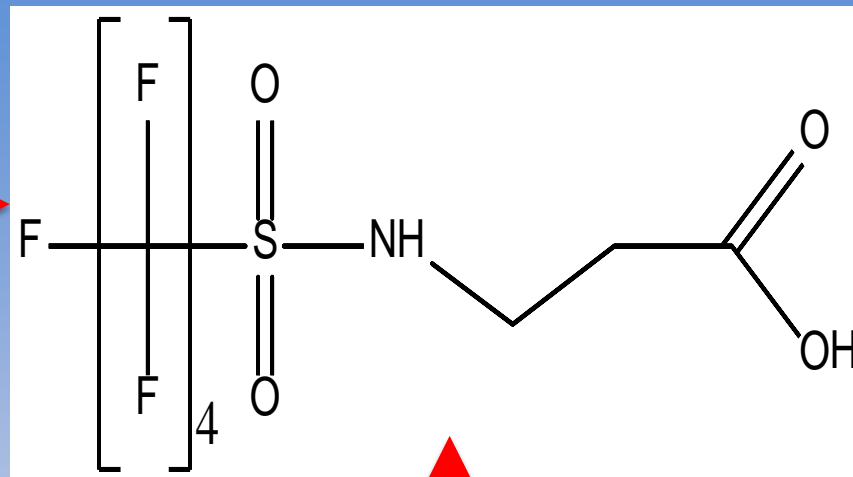
Possible proposed structure determined from:

- Accurate mass
- Isotope patterns
- Formula examination from Molecular Formula Generator (MFG)



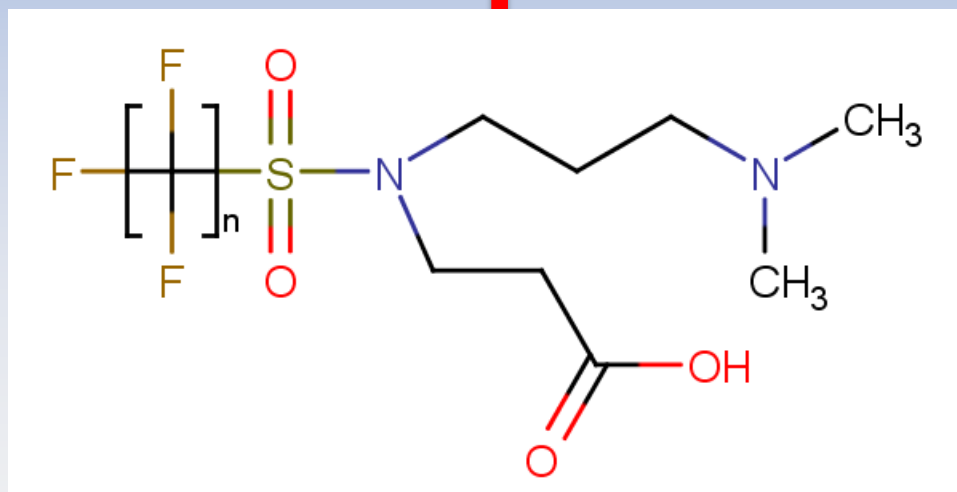
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Possible precursor:

- Perfluoroalkyl sulfonamide amino carboxylate ($n = 3-8$)
- Product of electrochemical fluorination process



References: Place and Fields (2012); D'Agostino and Mabury (2014)

Biomonitoring Research at ECL

- Non-targeted and semi-targeted methods give the opportunity to determine exposures not currently measured in targeted methods
- Non-targeted studies:
 - Investigating mother-infant transfer of chemicals of health concern using non-targeted methods (UCB, UCSF, DTSC)
 - Applying novel exposomic approaches for characterizing chemical exposure among women firefighters and nurses (UCB, Silent Spring, DTSC)
- New instrumentation

Biomonitoring Research at ECL

- Method development for targeted analysis
 - Online SPE automation of Expanded PFAS method
 - Addition of new PFAS compounds
 - Expanding current list of compounds
 - PFPeS, PFHpS, PFNS, 10:2 FTS, br-NMeFOSAA, br-NEtFOSAA
 - New replacement PFAS compounds
 - ADONA and F-53B
 - PFCHS

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- DTSC Biomonitoring Staff
- Biomonitoring California Staff

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