Exploring Point Sources of Poly- and Perfluoroalkyl Substances in California: Wastewater Treatment Plants, Air Force Bases, and Implications for CA Human Biomonitoring

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Outline

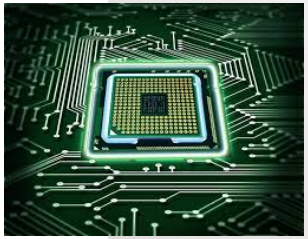
- Background on Poly- and Perfluoroalkyl Substances (PFASs)
- Methodology for aqueous samples
- PFASs in SF Bay wastewater effluent
- PFASs at 2 California AFBs
- Conclusions and Implications for Biomonitoring
- Expanding PFAS Measurement in Blood

Poly- and Perfluoroalkyl Substances (PFASs) in Consumer Products and Industrial Applications

Greaseproof coatings for paper and food wrappers (mainly historical)

Stain resistant and water repellent coatings

**Firefighting foams (AFFF)



**Electronics and Semiconductor Manufacturing

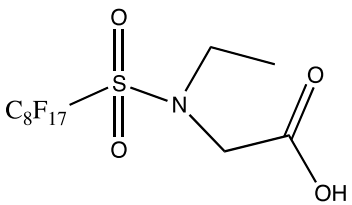
Manufacturing and Regulatory History

- 1950's – 2000's: C8 forms (PFOS and PFOA) were produced in the largest quantities
- 2002: PFOS phased out of US manufacturing
- 2006-2015: PFOA phased out by most US manufacturers
- 2009: PFOS is restricted under the Stockholm Convention
- 2009: Public Health Advisories for drinking water:

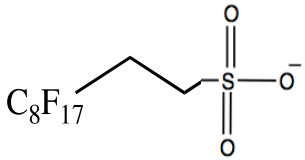
  200 ng/L PFOS, 400 ng/L PFOA (U.S. EPA)
- Presently: C6 and C4-based PFASs are most common – 6:2 fluorotelomers, PFHxA, PFPeA, PFBA, PFBS

Polyfluorinated vs. Perfluorinated

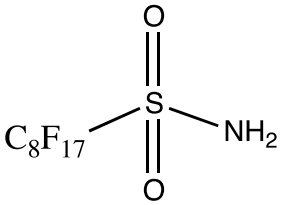
Molecules contain C-H bonds or other labile features



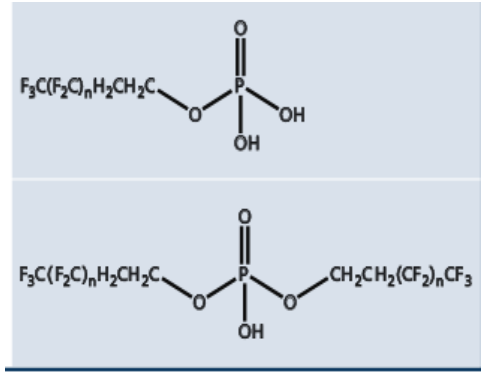
Et-FOSAA



8:2 fluorotelomer sulfonate

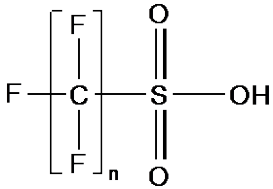


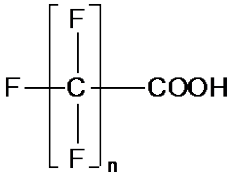
FOSA



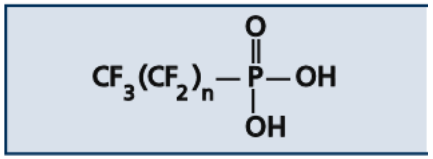
Mono- and diPAPs

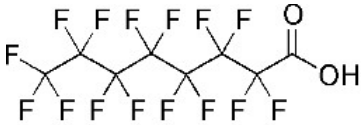
No C-H bonds



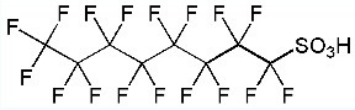


Perfluorinated sulfonic, carboxylic, and phosphonic acids





PFOA



PFOS

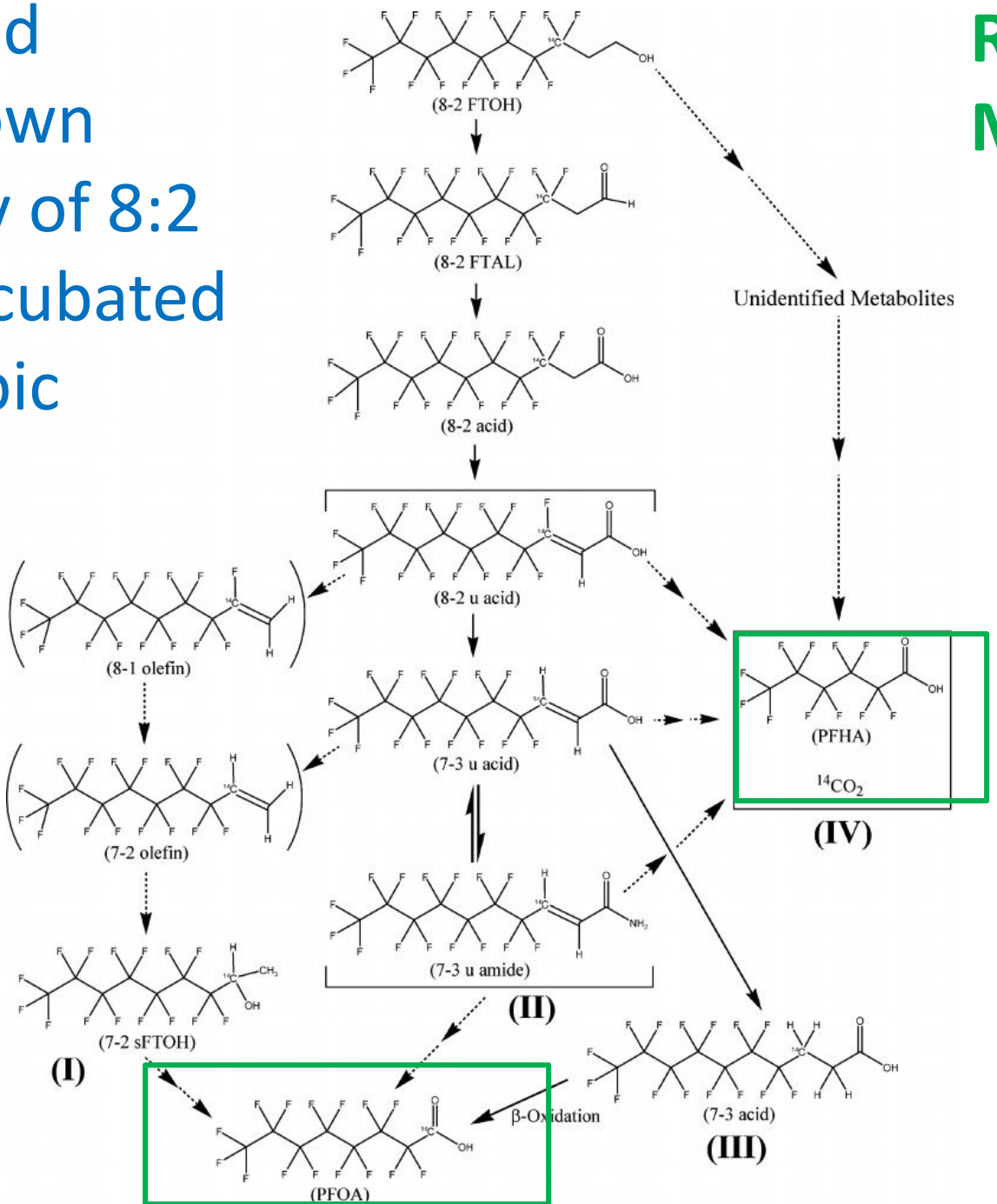
Polyfluorinated vs. Perfluorinated

- Some types can transform under environmental conditions
- Not much data on toxicology
- Precursors to perfluorinated acids
- Some are routinely measured, most are not

- Not susceptible to biological breakdown
- Terminal environmental products
- C8 forms and longer are very bioaccumulative, persistent, and toxic
- Easily and routinely measured

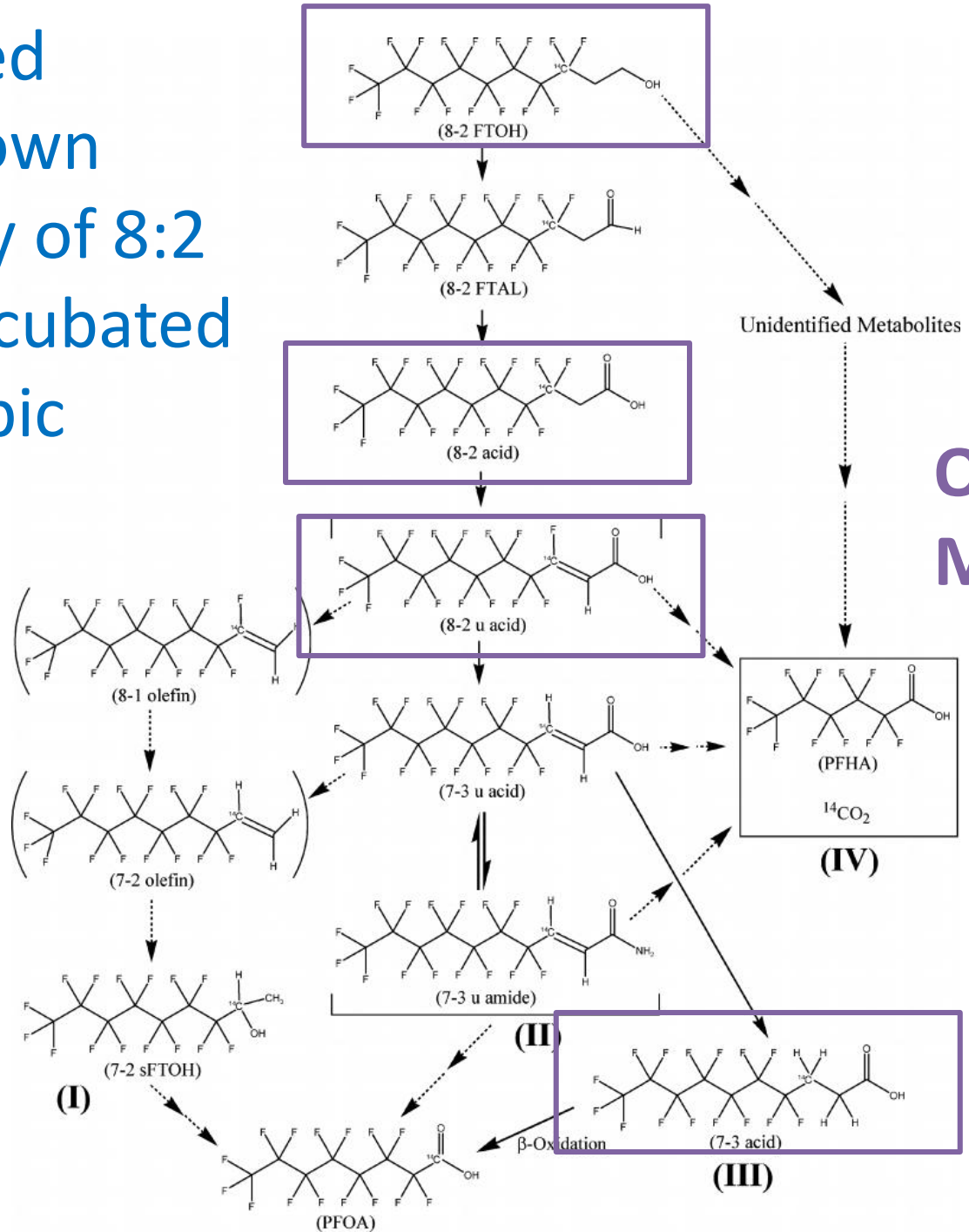
Proposed Breakdown Pathway of 8:2 FtOH incubated in Aerobic Sludge

Routinely Measured



Wang et al. 2005, ES&T

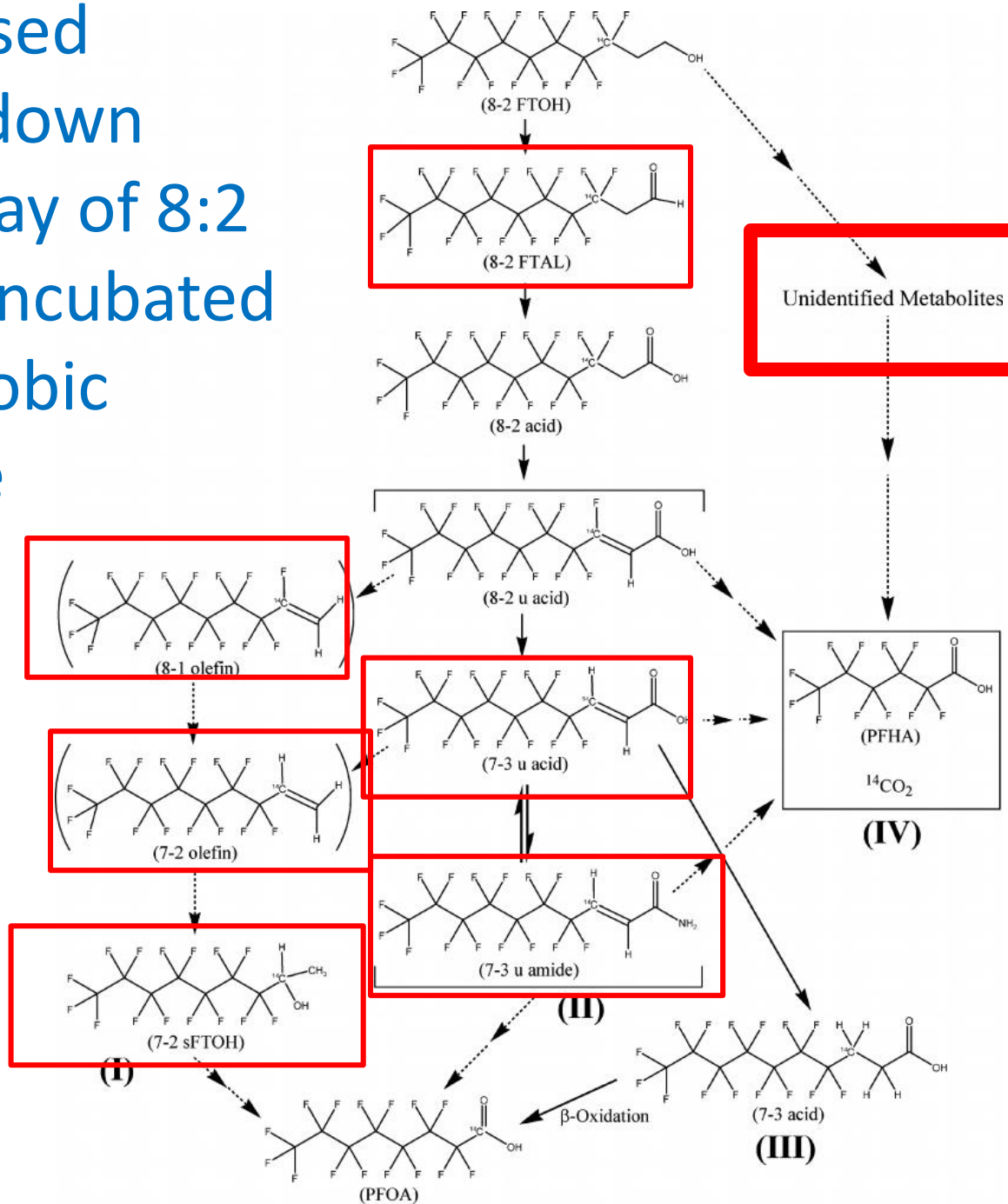
Proposed Breakdown Pathway of 8:2 FtOH incubated in Aerobic Sludge



Occasionally Measured

Wang et al. 2005, ES&T

Proposed Breakdown Pathway of 8:2 FtOH incubated in Aerobic Sludge



Can't be Quantified (no standards available)

Wang et al. 2005, ES&T

Methods: Wastewater and Groundwater

Direct Analysis of PFASs:

- Concentration of analytes via solid phase extraction (weak anionic exchange “WAX” cartridges)
  - Mass-labeled recovery standards added to sample before extraction
- Analysis on a UPLC-MS/MS system

Shimadzu Nexera UHPLC

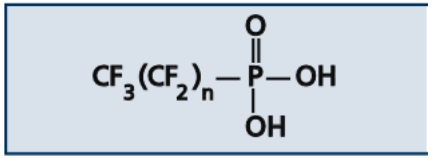
Waters Acquity BEH C18 Column

ABSciex 5500 QTrap

PFAS Analyte List: 40 chemicals

Perfluoroalkyl compounds

- C4 to C14 PFCAs perfluorinated carboxylates
- C4, C6, C8, C10 perfluorinated sulfonates
- C6 and C8 perfluorinated phosphonates

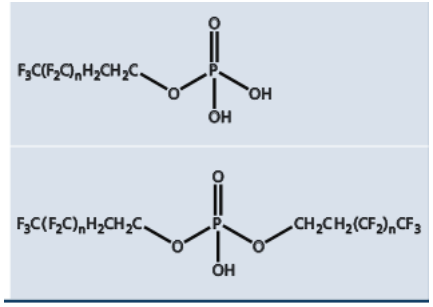


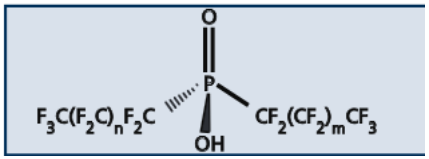
Polyfluoroalkyl compounds ("Precursors")

- 4:2, 6:2, 8:2 fluorotelomer sulfonates
- C6, C8 fluorotelomer acids
- C6 and C8 mono- and di-PAPs
- C8 perfluorinated sulfonamido compounds

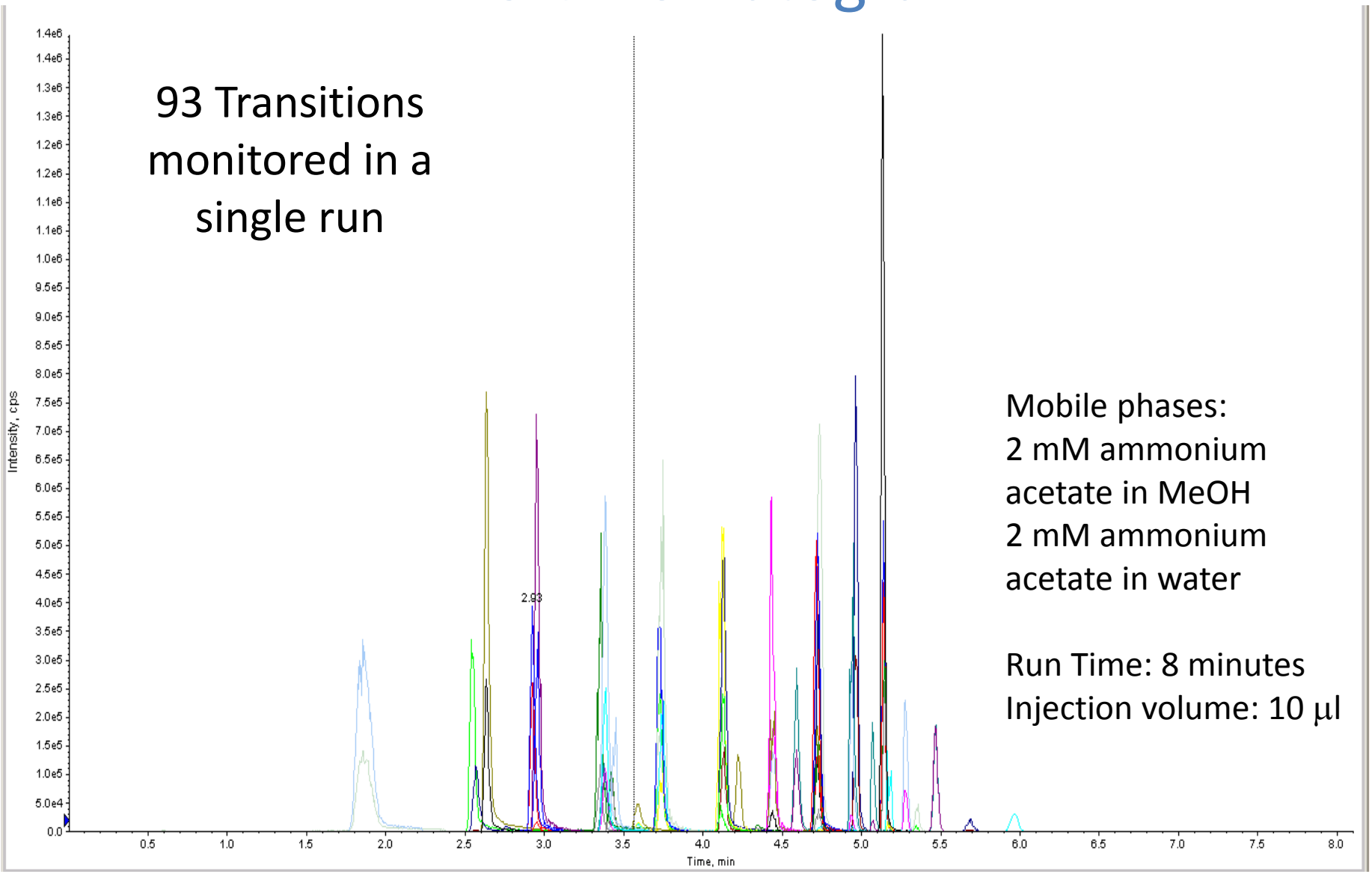
(FOSA, EtFOSAA, SAmPAP, diSAmPAP)

- 6:6, 6:8, and 8:8 perfluorophosphinates

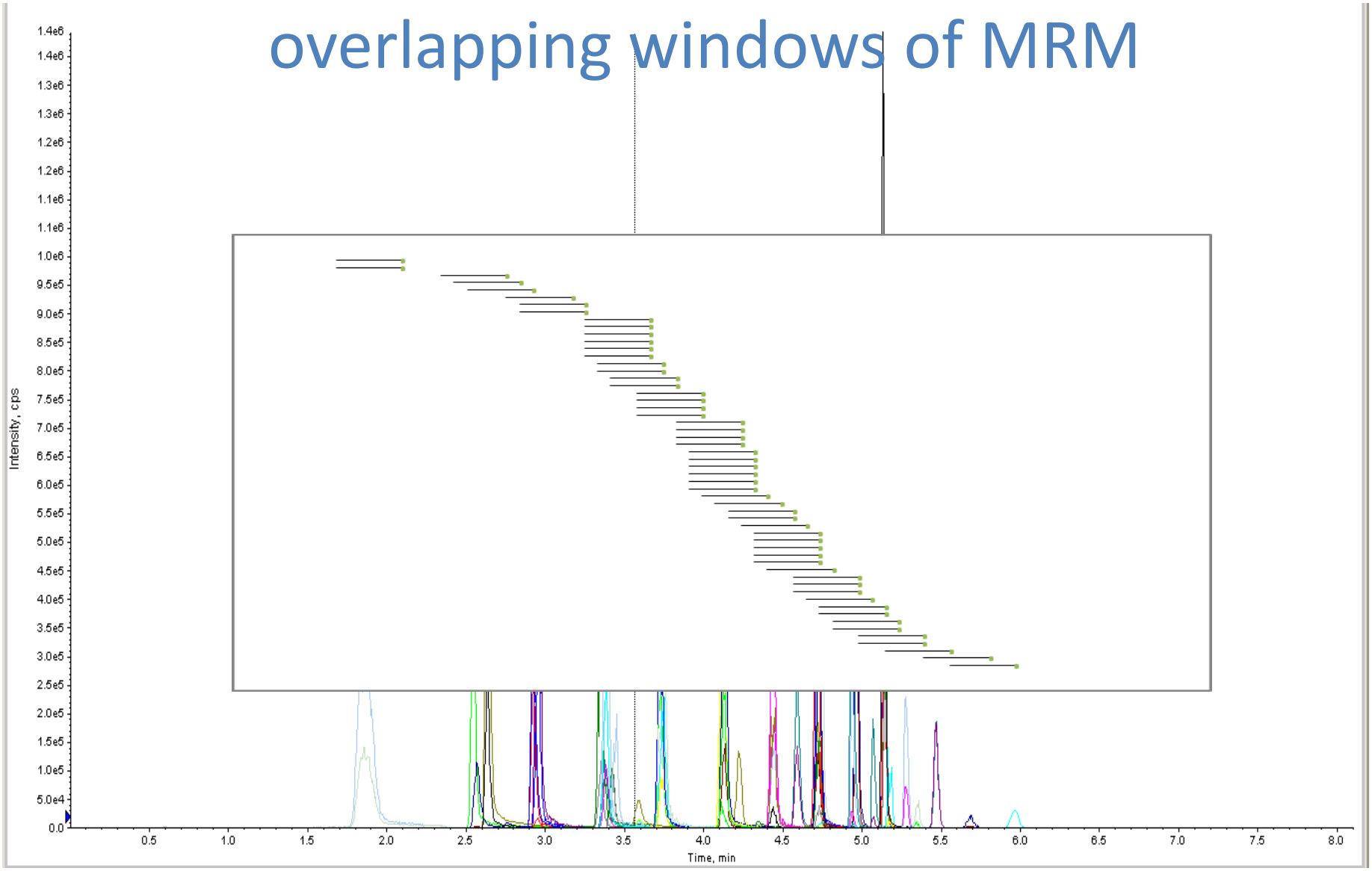




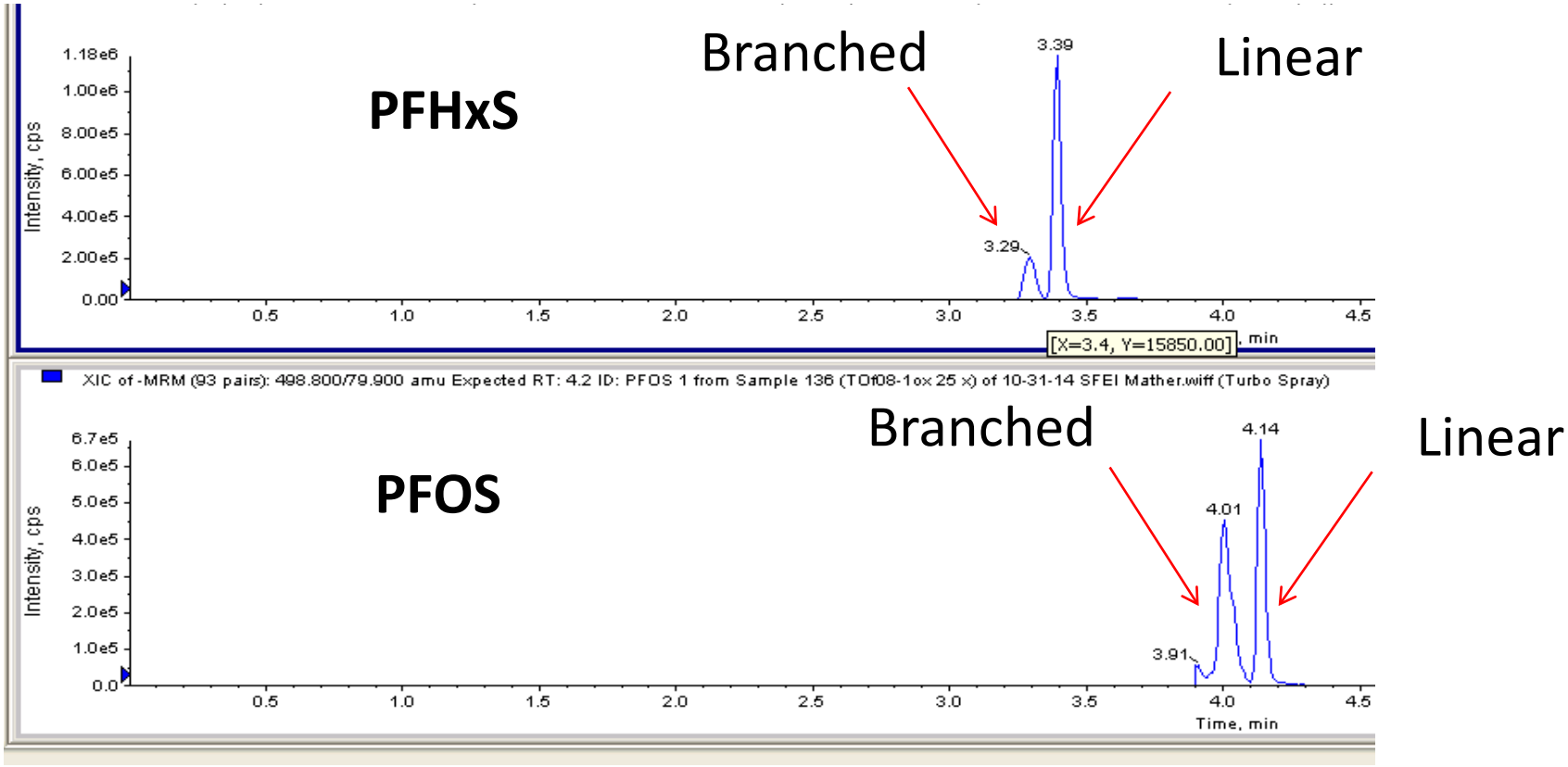
PFAS Chromatogram



Scheduled MRM feature in Analyst enables overlapping windows of MRM



Clear Isomer Separation on C18 column (1.7µm, 2.1 mm) under UPLC conditions



*Chromatogram from wastewater sample

Instrumental LOD and LOQ

	Instrumental LOD	Instrumental LOQ
	ng/L	ng/L
42 FtS	1.6	2.7
62 FtS	2.8	4.6
82 FtS	2.4	3.9
62 diPAP	4.9	8.1
82 diPAP	6.8	11
62 PAP	52	87
82 PAP	480	800
66 PFPi	1.0	1.6
68 PFPi	3.5	5.8
88 PFPi	4.5	7.5
diSAmPAP	4.7	7.9
FOSA	2.0	3.3
MeFOSAA	2.8	4.7
EtFOSAA	2.1	3.4
FPePA	5.7	9.5
FHpPA	5.8	9.7
FHEA	73	120
FHUEA	4.3	7.1
FOEA	120	210
FOUEA	2.3	3.9

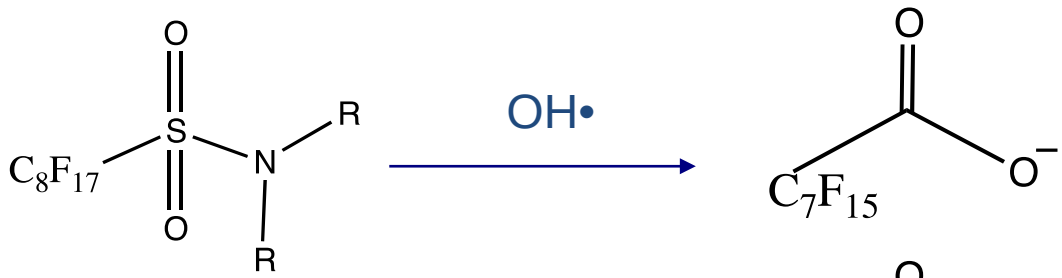
	Instrumental LOD	Instrumental LOQ
	ng/L	ng/L
PFHxPA	2.0	3.3
PFOPA	2.8	4.6
PFBS	1.9	3.1
PFHxS	2.0	3.4
PFOS	1.4	2.4
PFDS	2.7	4.5
PFBA	2.0	3.4
PFPeA	9.3	15
PFHxA	4.1	6.9
PFHpA	2.9	4.8
PFOA	6.2	10
PFNA	8.1	13
PFDA	8.9	15
PFUA	12	20
PFDoA	23	39
PFTrA	18	30
PFTeA	34	57

Methods

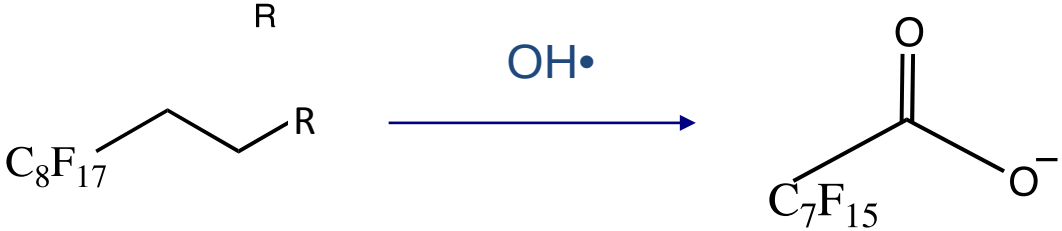
Indirect Measurement of Polyfluorinated "Precursor" Compounds

- Samples are oxidized with OH using heat activated persulfate
- Polyfluorinated compounds are transformed to perfluorinated carboxylates (PFCAs)
- **Molar production of PFCAs is equivalent to molar concentration of polyfluorinated compounds**

Perfluorinated Sulfonate Precursors



Perfluorinated Carboxylate Precursors



+ shorter PFCA products

$\Sigma\ \Delta$ [PFCAs] ~ [Polyfluorinated Compounds]

WWTP Study Objectives

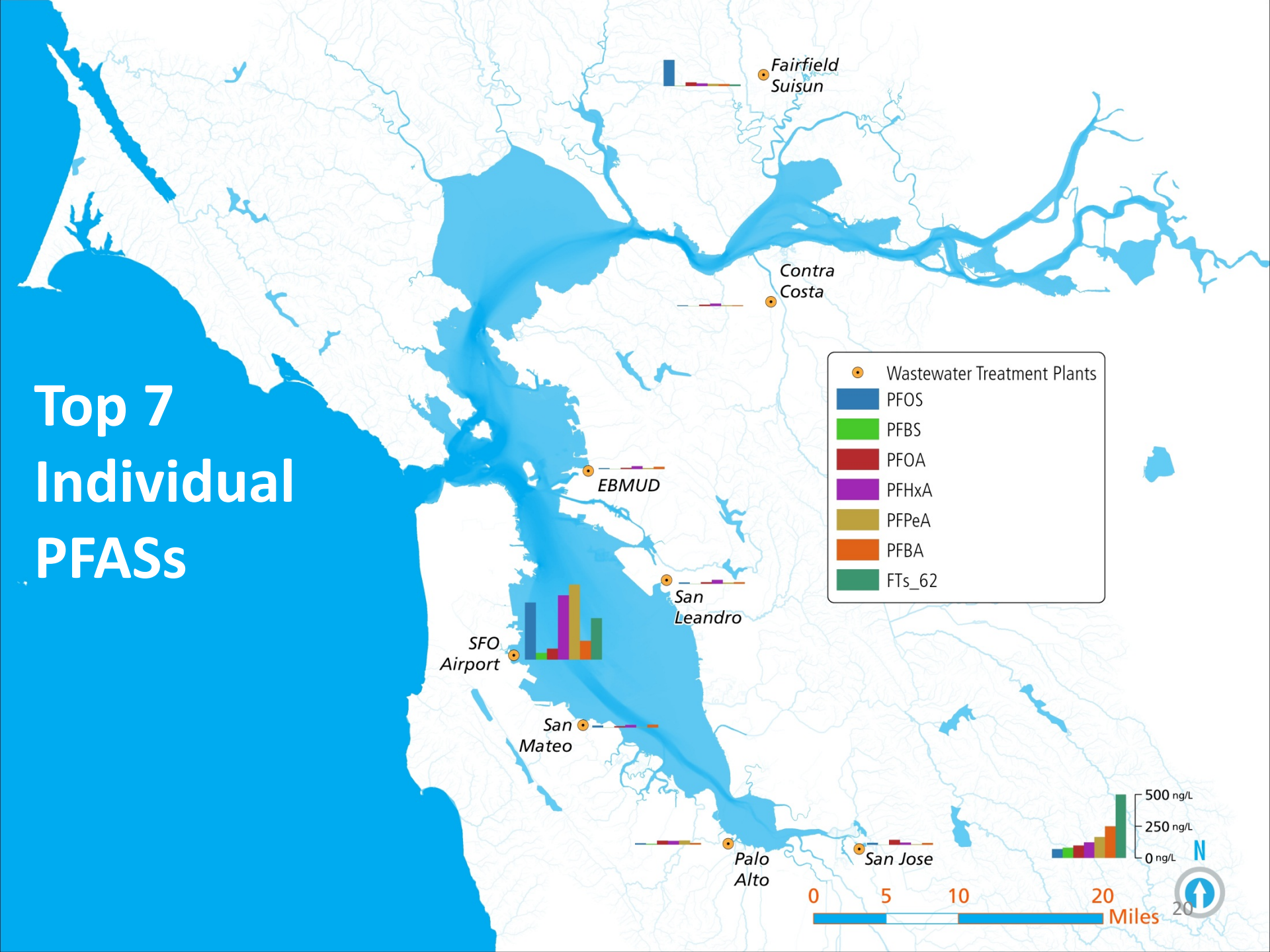
- Characterize PFAS profiles and concentrations in wastewater effluent from treatment plants around SF Bay
  - Identify hot spots
  - Identify changing profiles of PFASs
- Quantify the total concentration of polyfluorinated compounds that might be precursors to perfluorinated acids
  - Assess the potential of wastewater to serve as a future source of perfluorinated acids such as PFOS, PFOA

Sampling

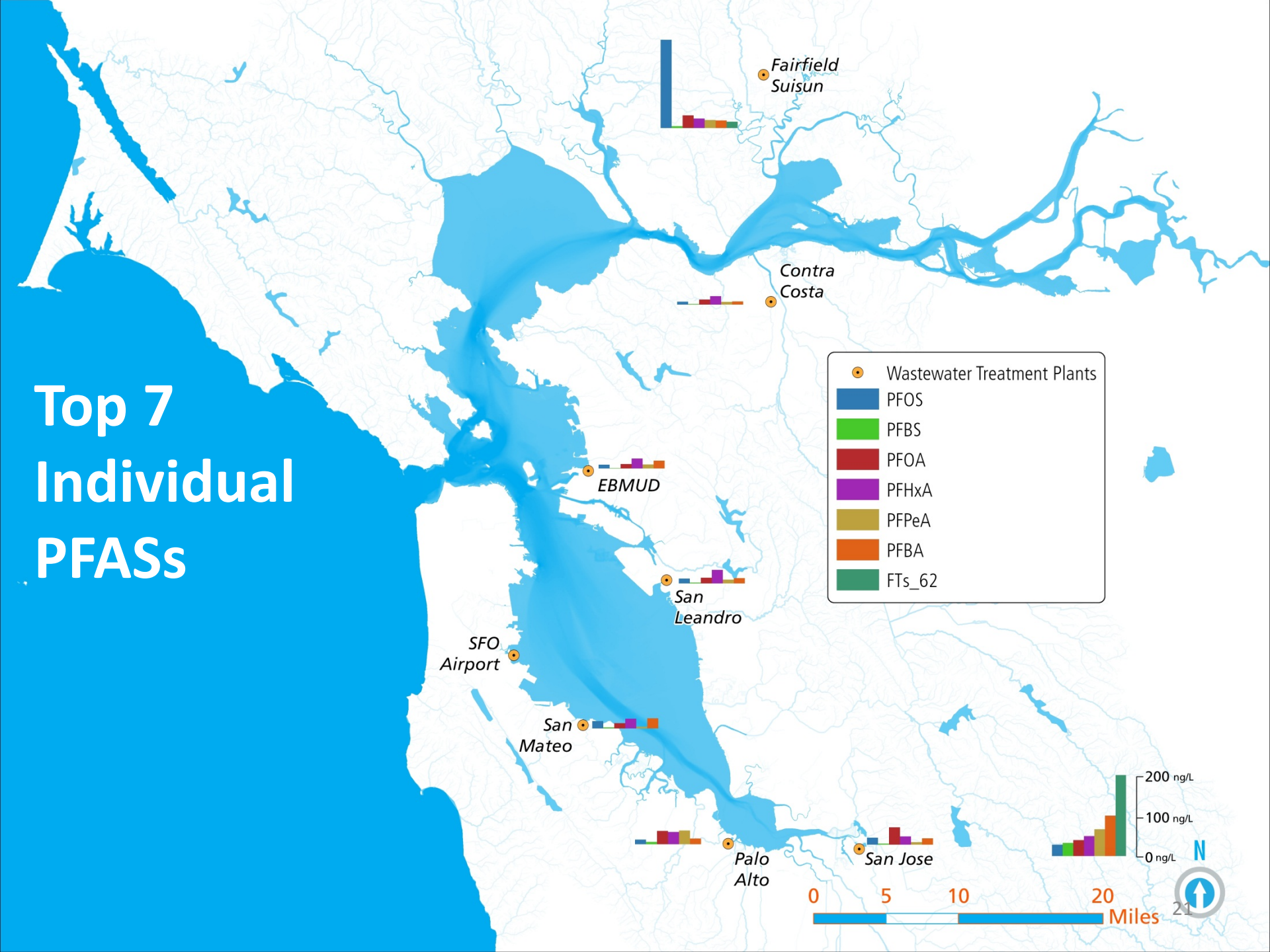
- 8 wastewater plants
  - Final effluent
  - 1 equipment blank
  - 1 sampling duplicate (EBMUD)
  - Received by ECL with blind IDs
- Sampling occurred in early fall 2014 during dry weather

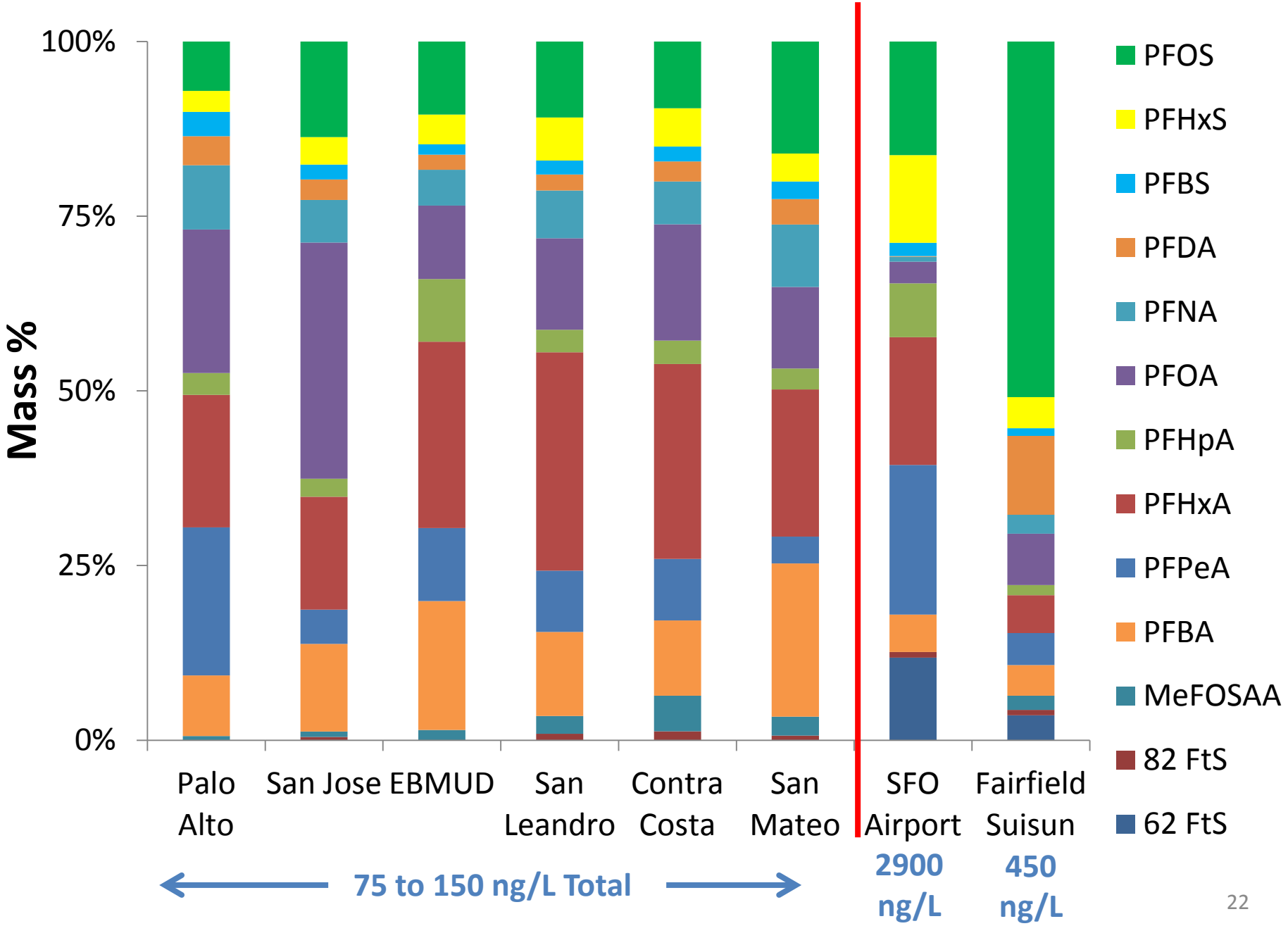
Location	Treatment Load, Dry weather avg. (mgd)	Tertiary Treatment	Inputs to Consider
Fairfield Suisun	12.2	Filtration, UV disinfection	Travis Air Force Base
Contra Costa	45	UV disinfection	
EBMUD	75		Oakland Airport, Older industrial inputs
San Leandro	5		High TSS Load in Effluent
San Francisco Airport - Industrial	0.63		Firefighting foams from runways
San Mateo	12	Sometimes filters	
Palo Alto	25	Filtration	
San Jose	80	Filtration	San Jose Airport, semiconductor manufacturing

Top 7 Individual PFASs

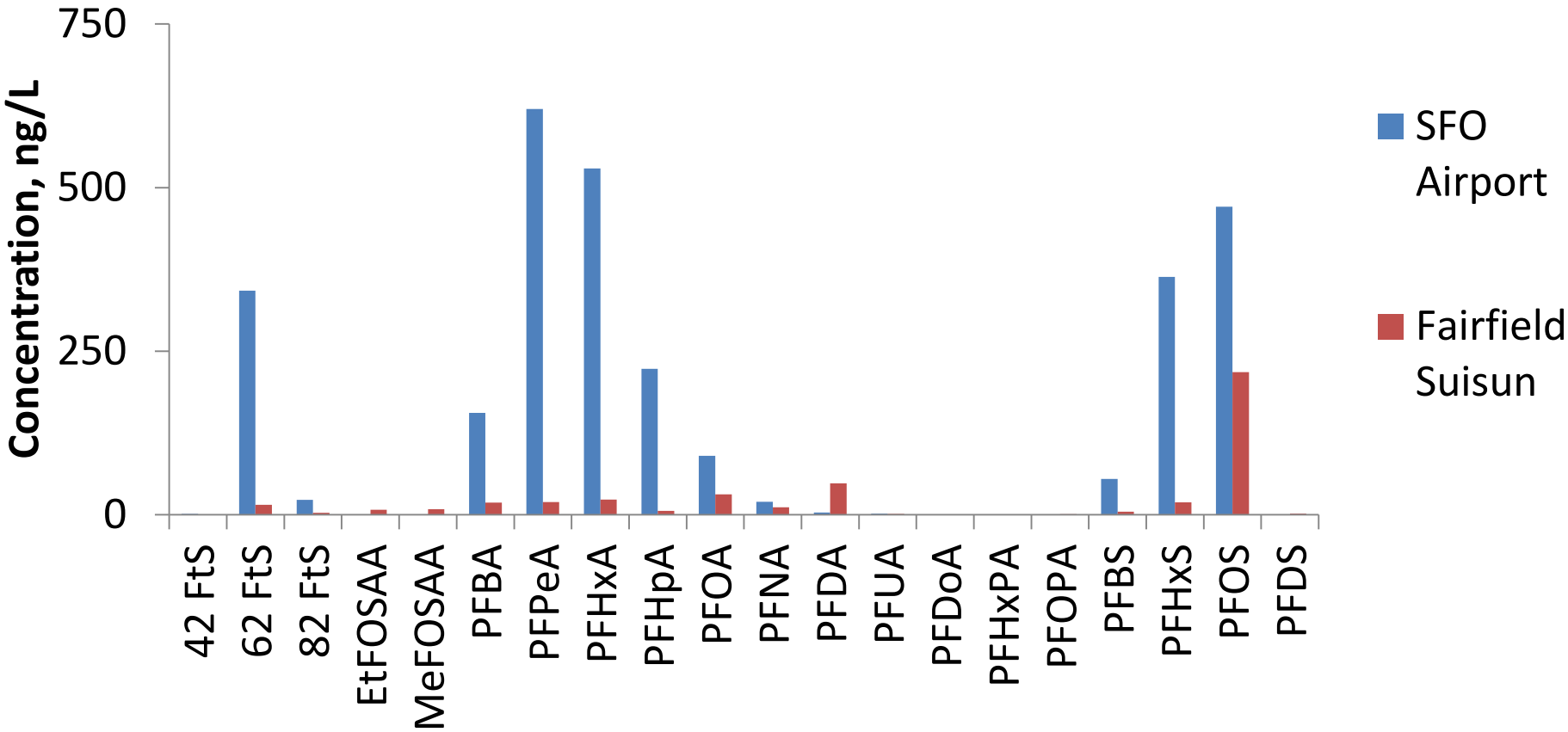


Top 7 Individual PFASs

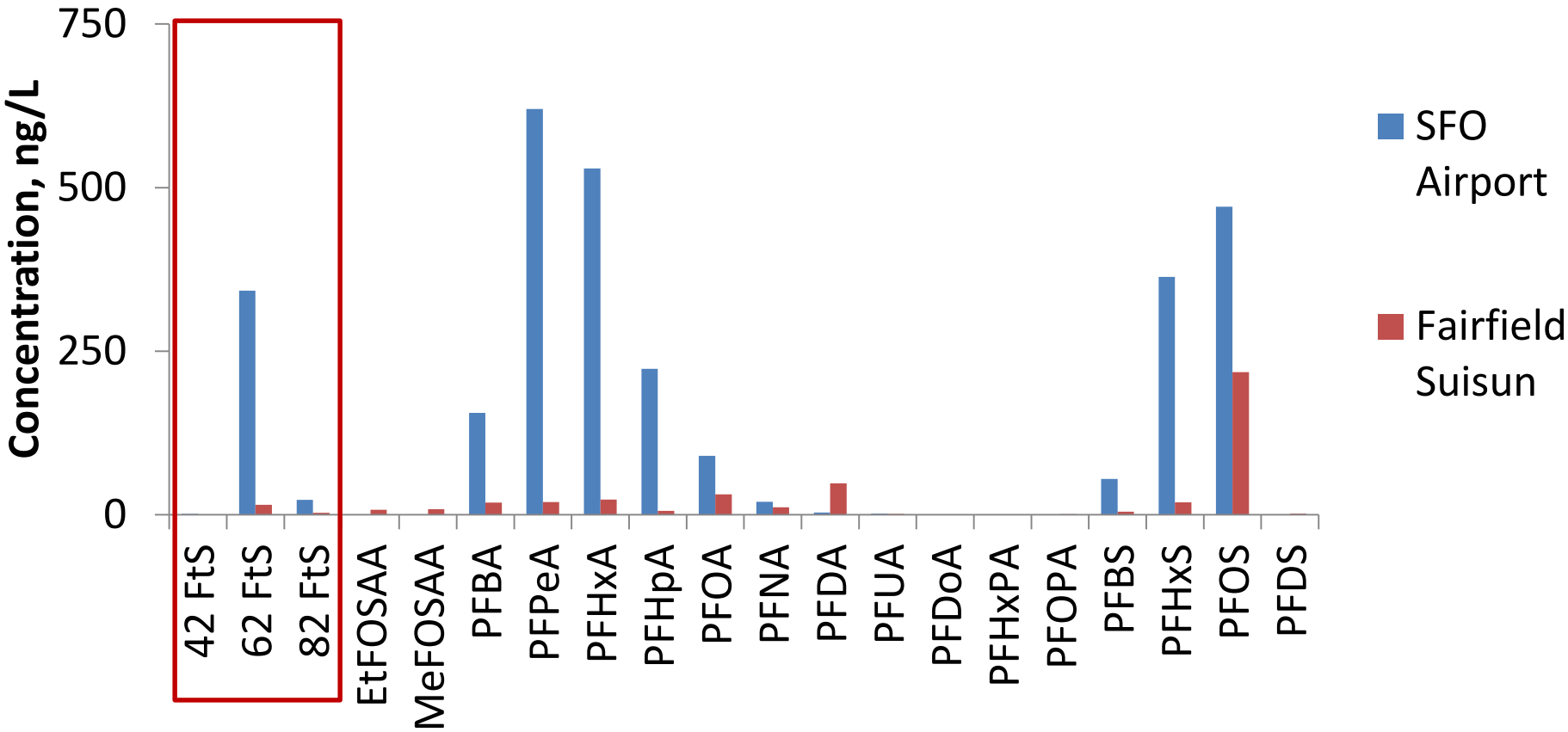



100%
75%
50%
25%
0%
Mass %
Palo Alto
San Jose
EBMUD
San Leandro
Contra Costa
San Mateo
SFO Airport
Fairfield Suisun
PFOS
PFHxS
PFBS
PFDA
PFNA
PFOA
PFHpA
PFHxA
PFPeA
PFBA
MeFOSAA
82 FtS
62 FtS
75 to 150 ng/L Total
2900 ng/L
450 ng/L

SFO Airport Industrial and Fairfield Suisun

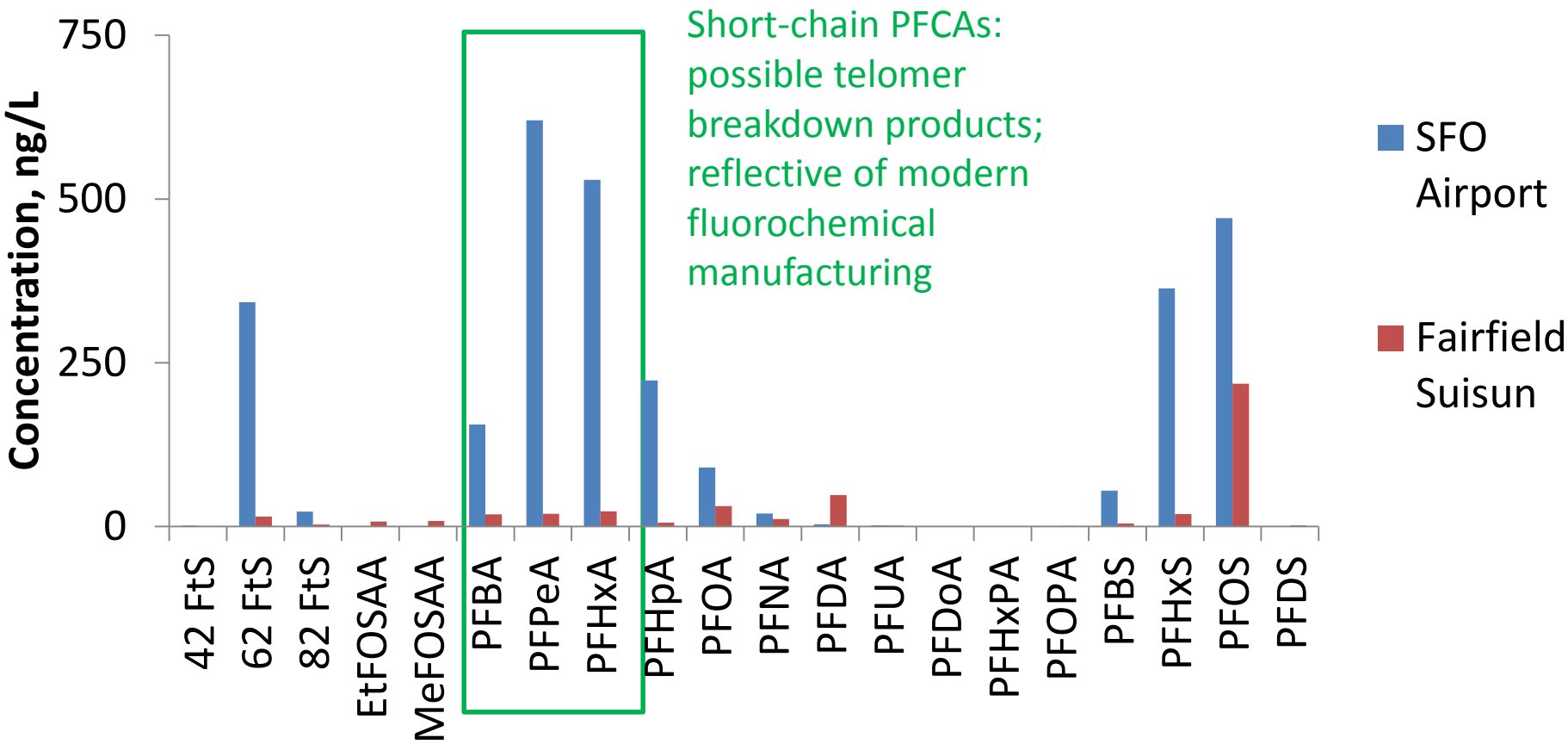


SFO Airport Industrial and Fairfield Suisun

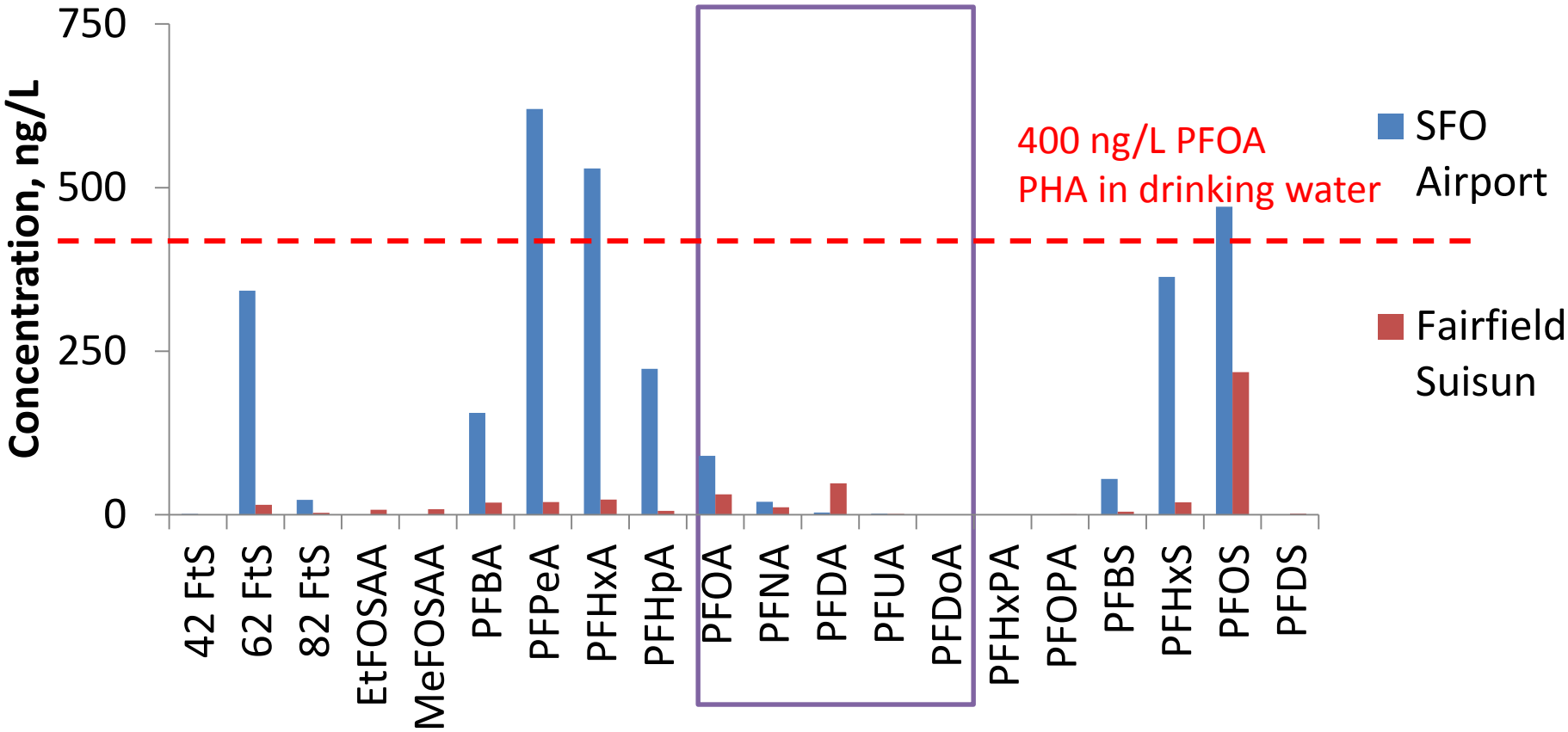


Fluorotelomer sulfonates (FtSs) indicative of firefighting foam contamination

SFO Airport Industrial and Fairfield Suisun

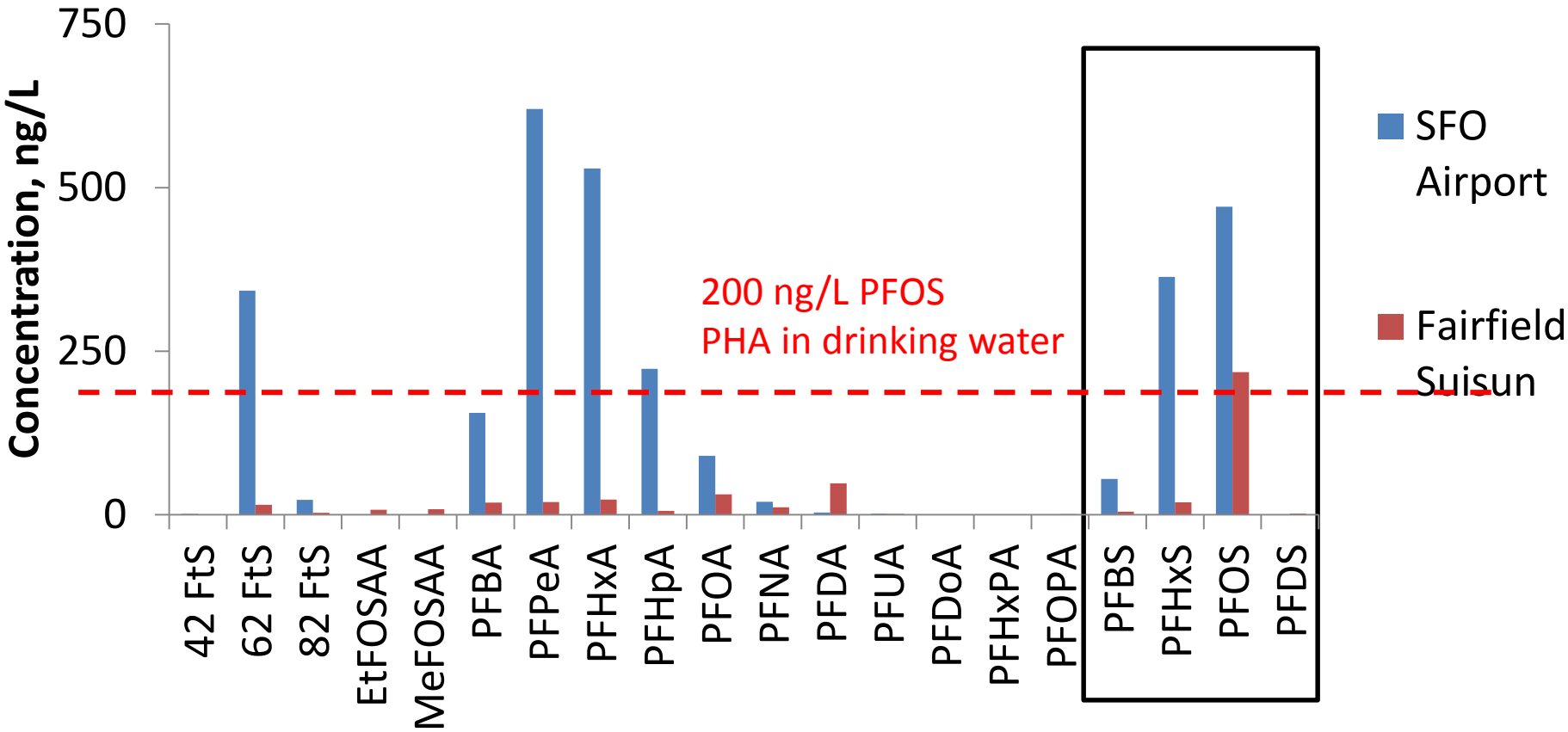


SFO Airport Industrial and Fairfield Suisun



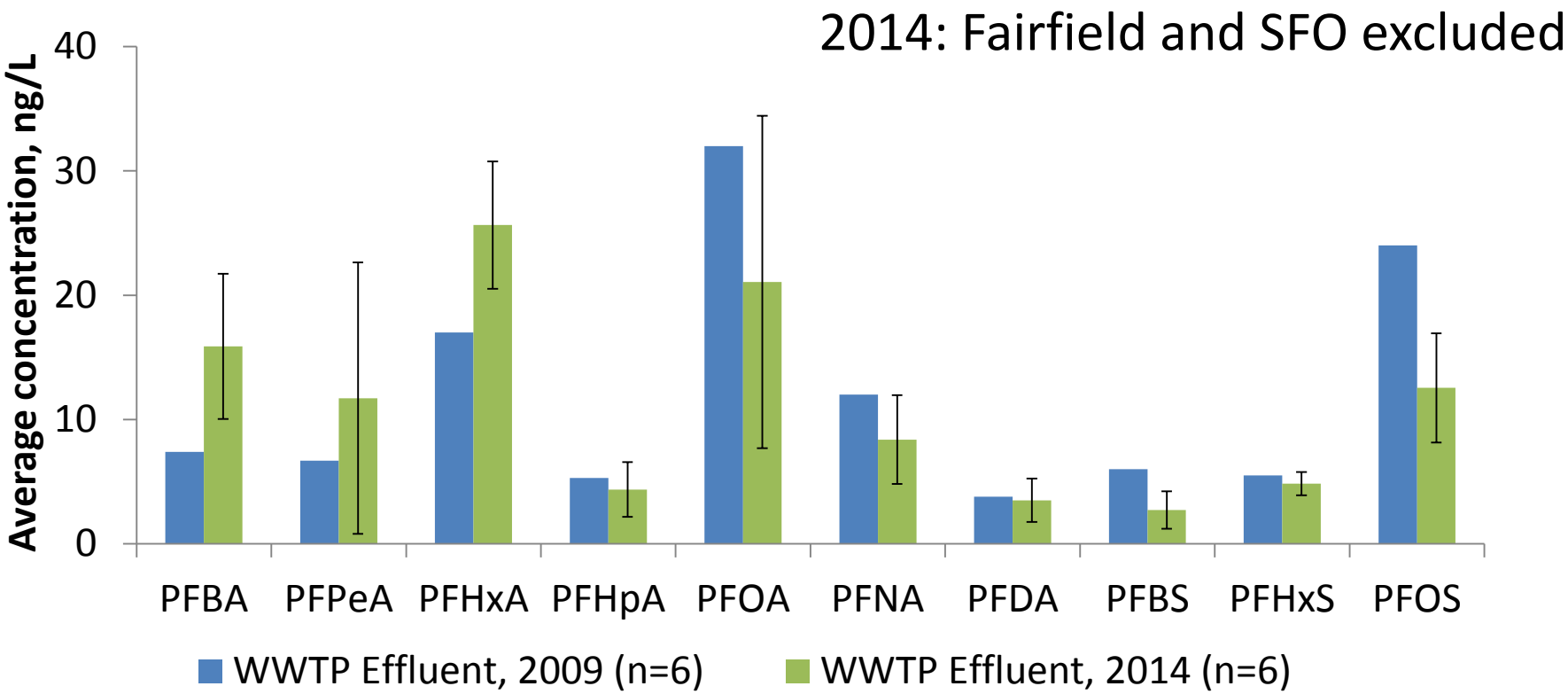
Long-chain PFCAs associated with historical fluorochemical manufacturing

SFO Airport Industrial and Fairfield Suisun



PFSAs: associated with firefighting foams but also many consumer products uses

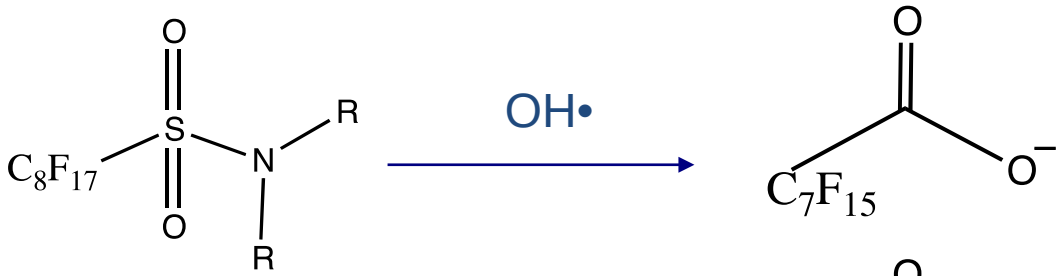
SF Bay PFAS Profiles in WWTP Effluent: 2009 vs. 2014



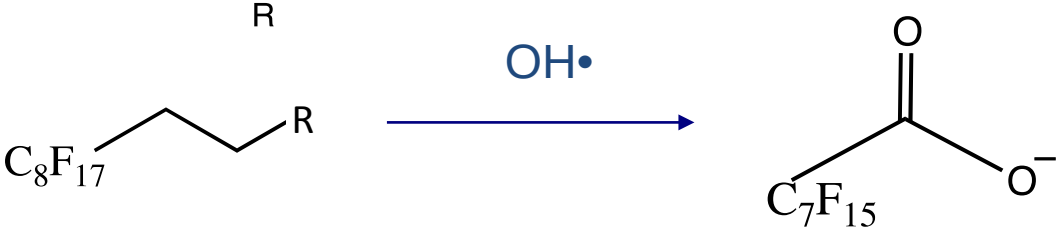
2009 source: Contaminants of Emerging Concern in SF Bay: A Summary of Occurrence Data and Identification of Data Gaps, Klosterhaus et al. 2013

Indirect Measurement of Polyfluorinated Compounds

Perfluorinated Sulfonate Precursors



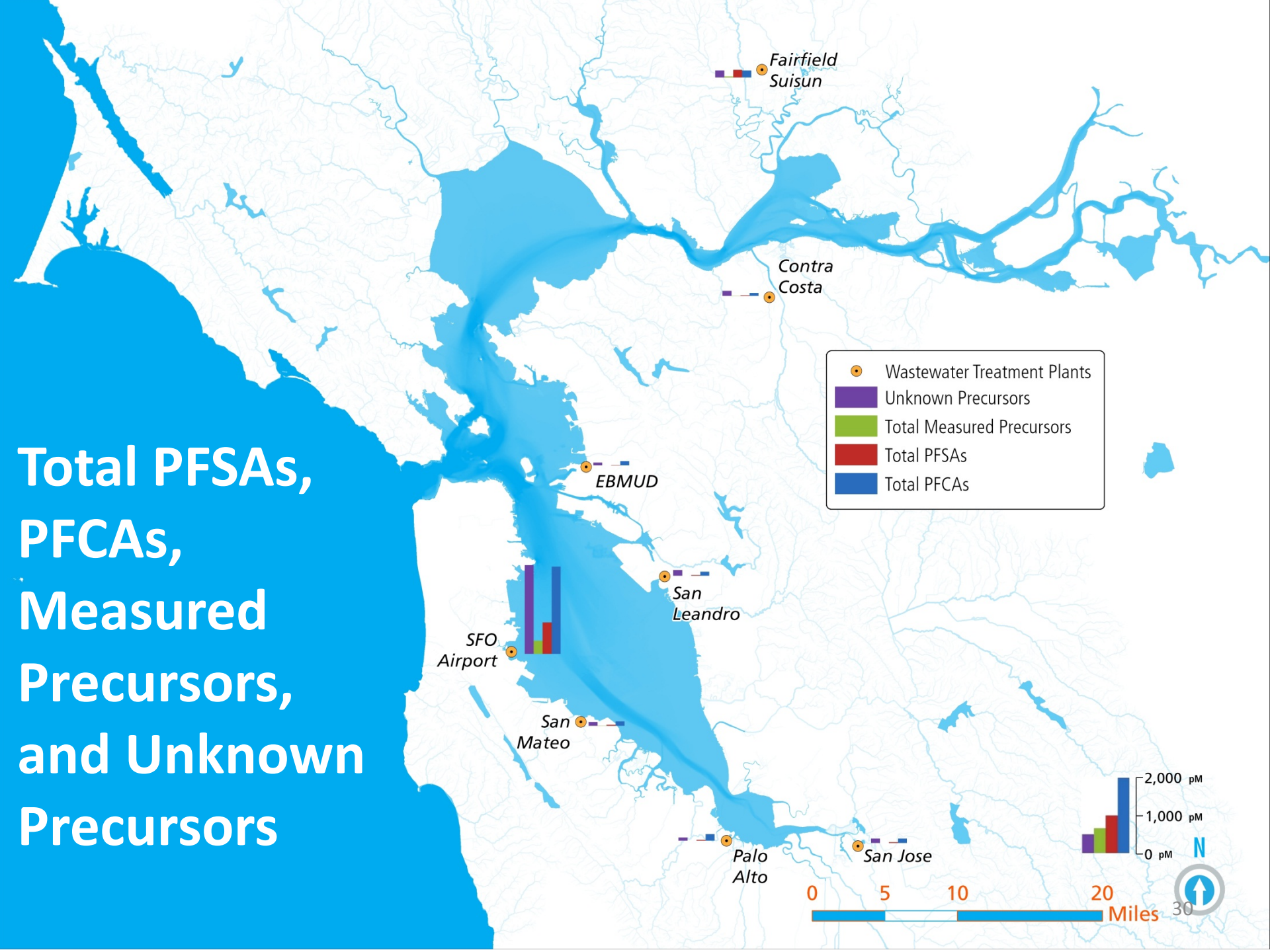
Perfluorinated Carboxylate Precursors



+ shorter PFCA products

$\Sigma\ \Delta$ [PFCAs] ~ [Polyfluorinated Compounds]

Total PFSAs, PFCAs, Measured Precursors, and Unknown Precursors



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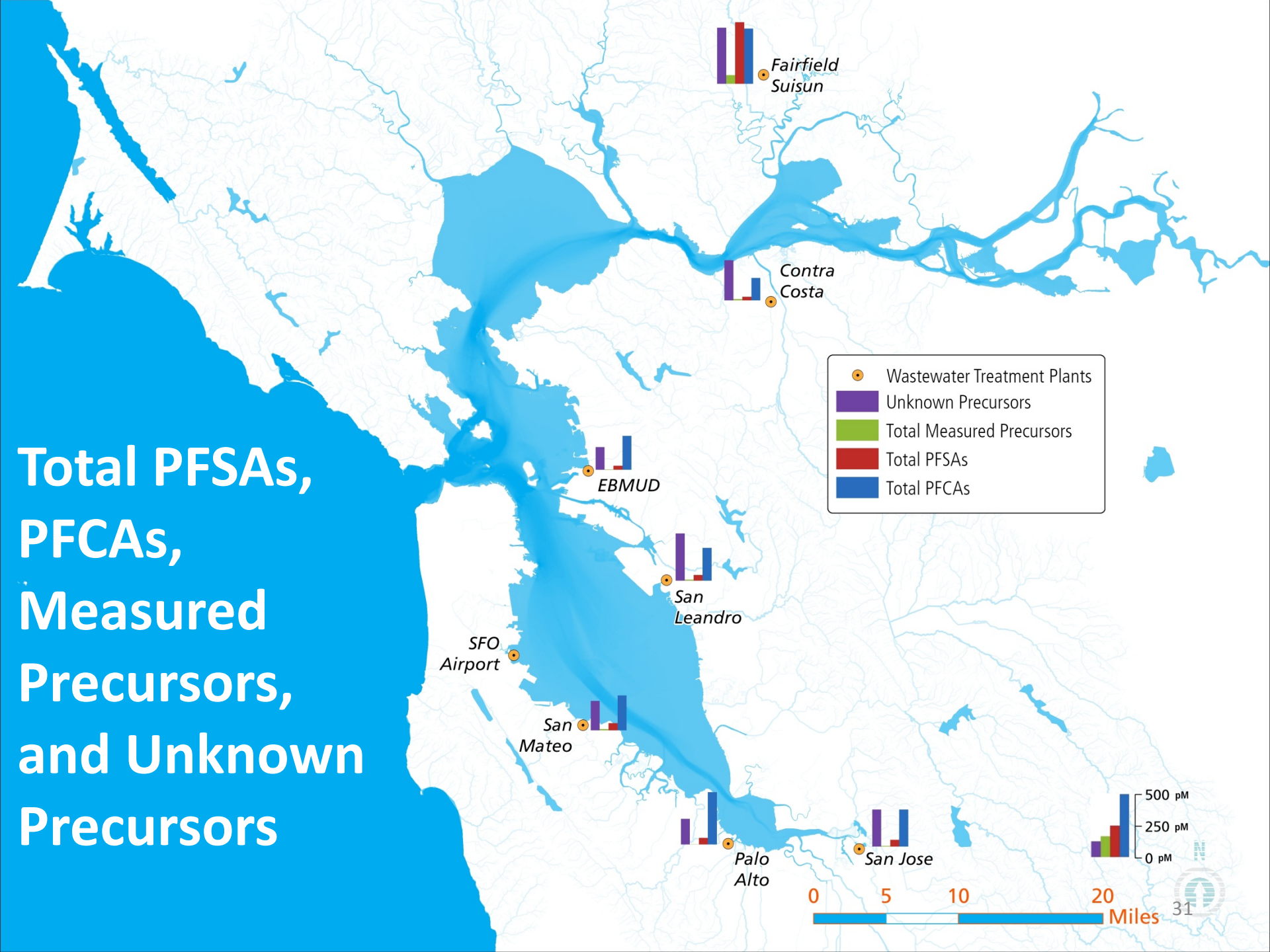
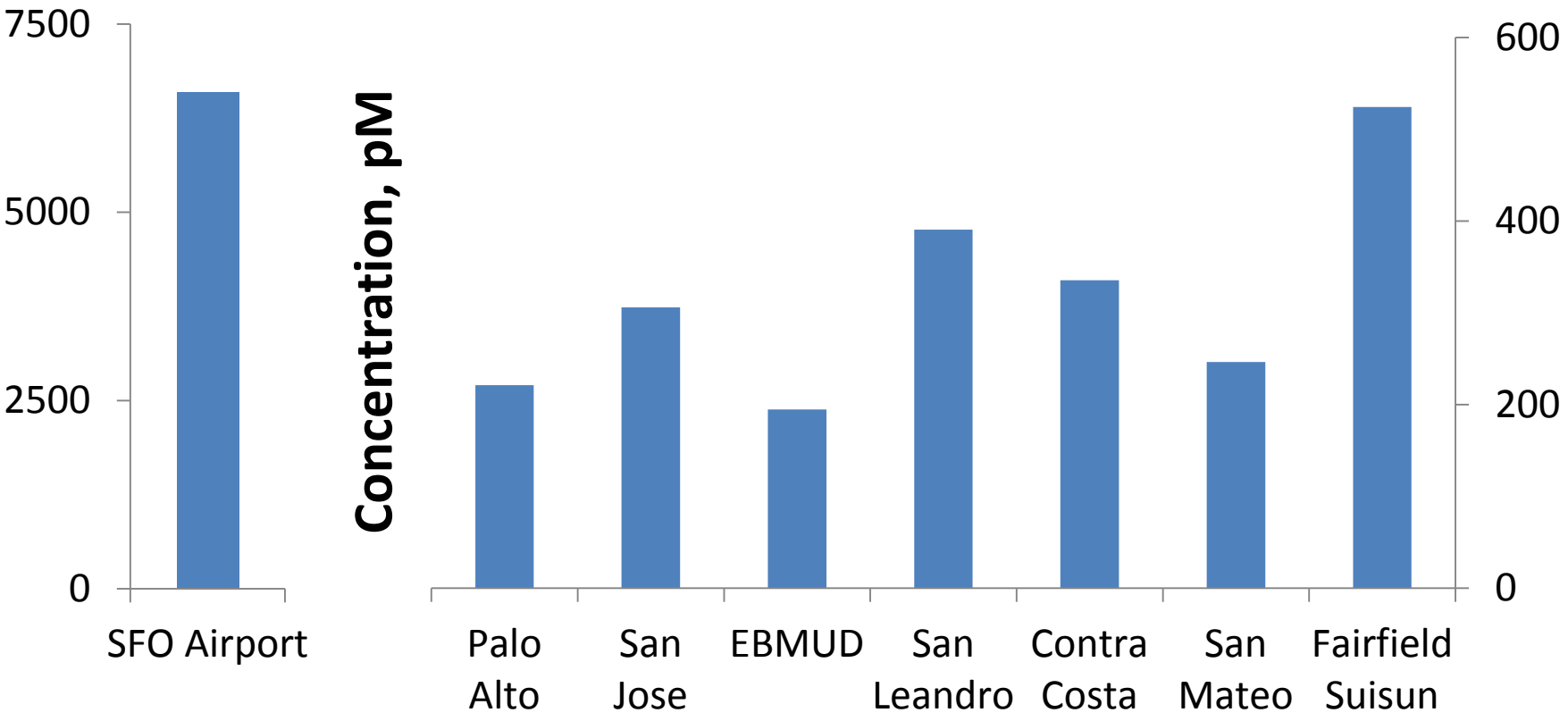
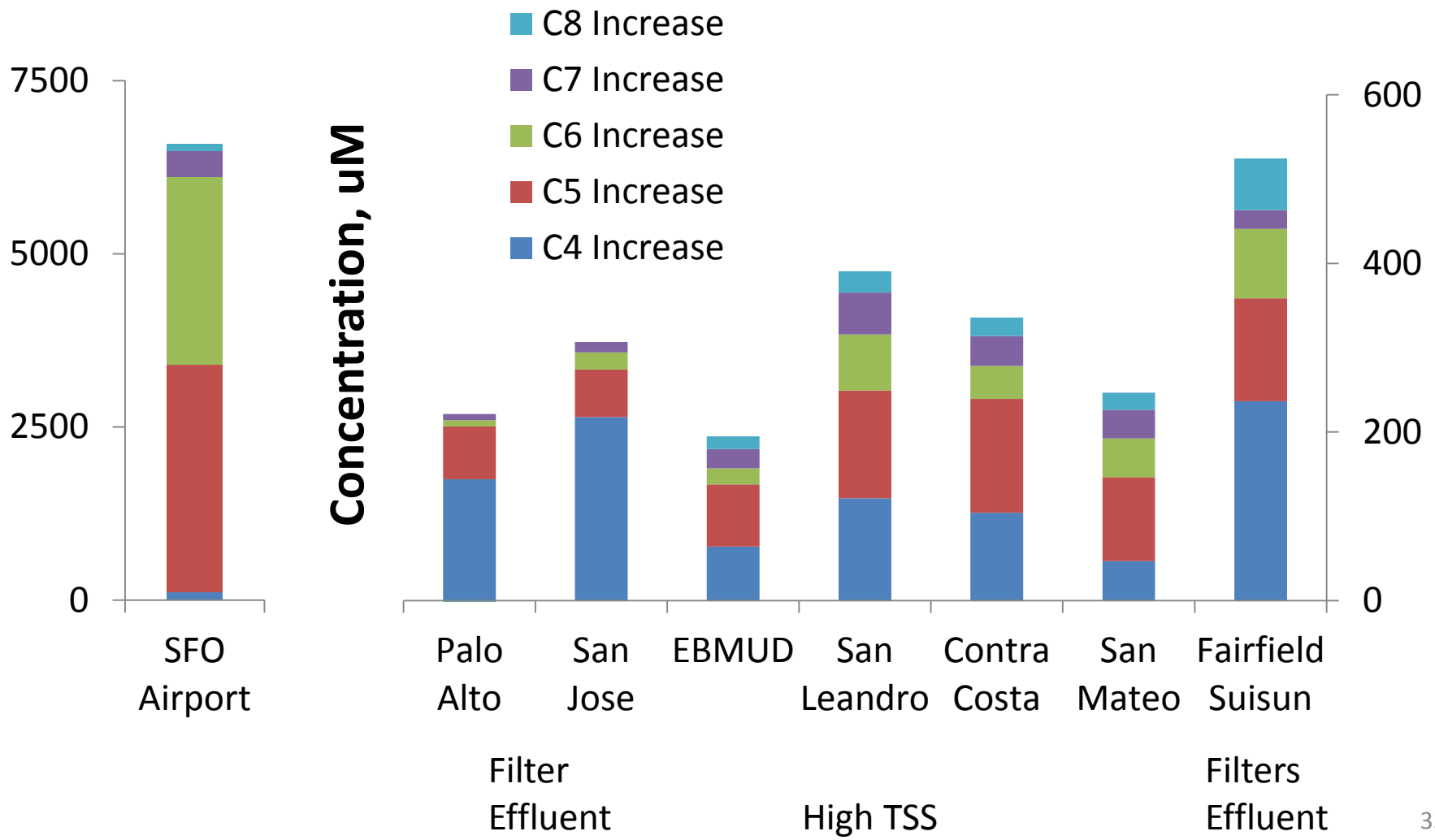


Total Polyfluorinated Compounds



Total Polyfluorinated Compounds



Wastewater Treatment Plants: Individual Conclusions

Location	Inputs to Consider
Fairfield Suisun	High PFOS inputs; PFASs associated with AFFF; Polyfluorinated profile resembles other municipal WWTPs
Contra Costa	Lowest [PFASs]
East Bay MUD	
San Leandro	Slightly higher [C8 poly] compounds, possibly related to TSS?
San Francisco Airport - Industrial	Most contaminated, highest [PFASs]
San Mateo	
Palo Alto	Lowest polyfluorinated fraction of PFASs; minimal C8 precursors
San Jose	Minimal C8 precursors

Overall Conclusions for SF Bay WWTPs

- Shorter chain perfluorinated carboxylates appear to have risen in concentration in WWTP effluent since 2009 and predominate in many samples; PFOS and PFOA appear to have declined

- Short chain polyfluorinated compounds also predominate

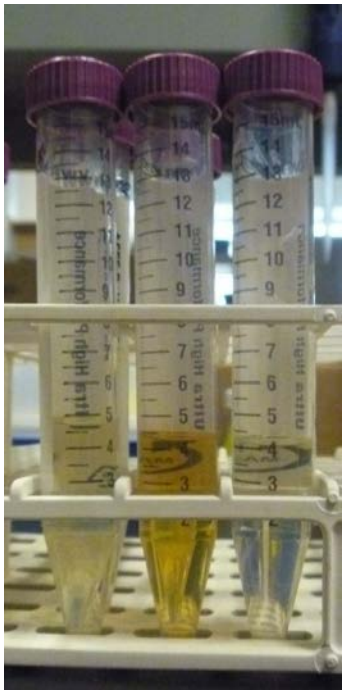
- Airport industrial runoff and AFBs are a source of high concentrations and unique profiles of PFASs in effluent

Air Force Bases

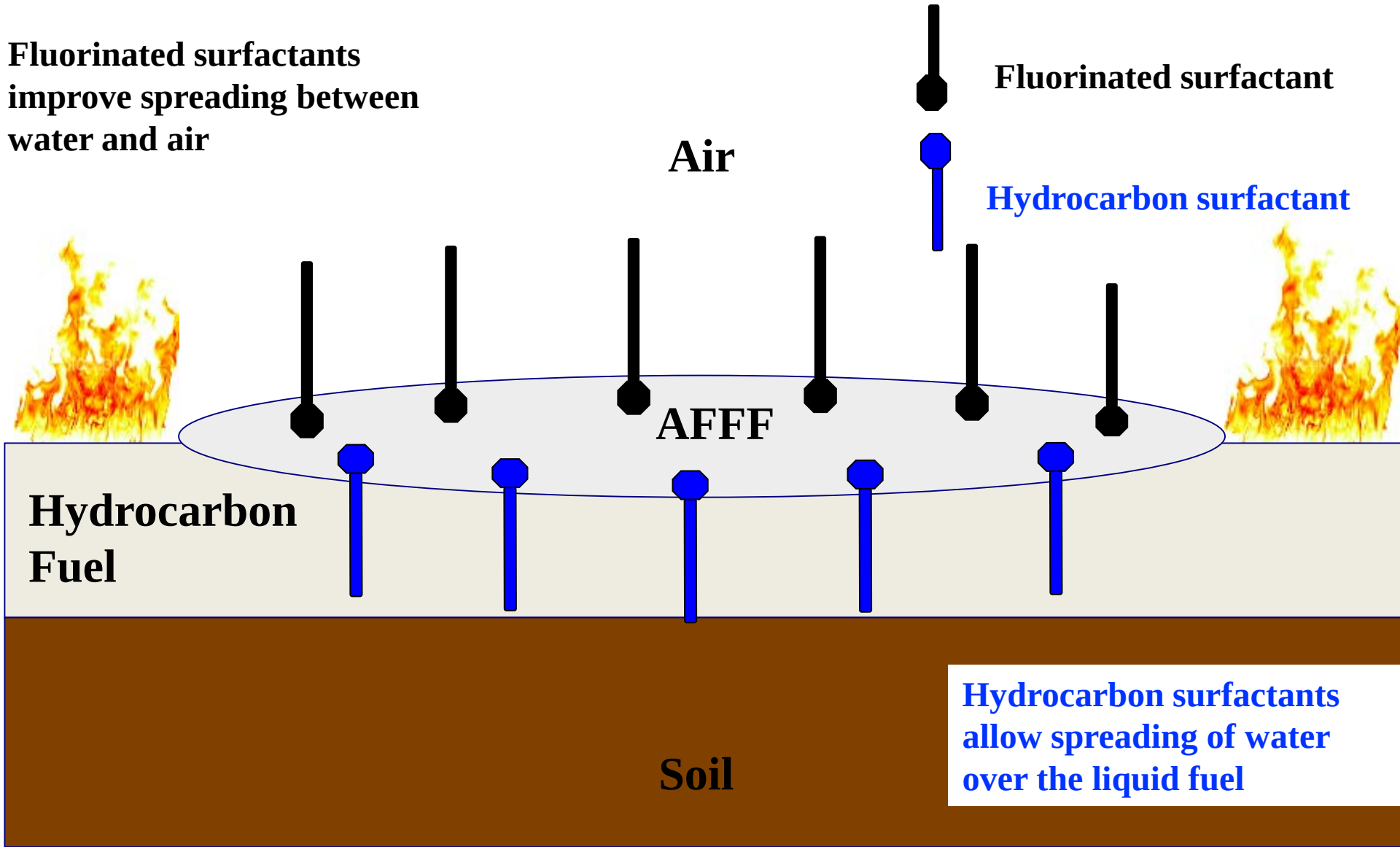
- Air Force Civil Engineering Center (AFCEC) commissioned studies of PFASs in groundwater and soil at Air Force Bases (AFBs) with fire training areas
- Fire training areas are well-established point sources of PFASs
- Groundwater from these sites are often already treated for other contaminants such as VOCs

Aqueous Film Forming Foams (AFFF)

- Used by municipalities, airports, refineries, and military personnel to extinguish fuel-based fires
- Hydrocarbon and fluorocarbon surfactants are the active ingredients
- Repeated use* and accidental spills have led to large contamination of PFASs in underlying groundwater and sediments

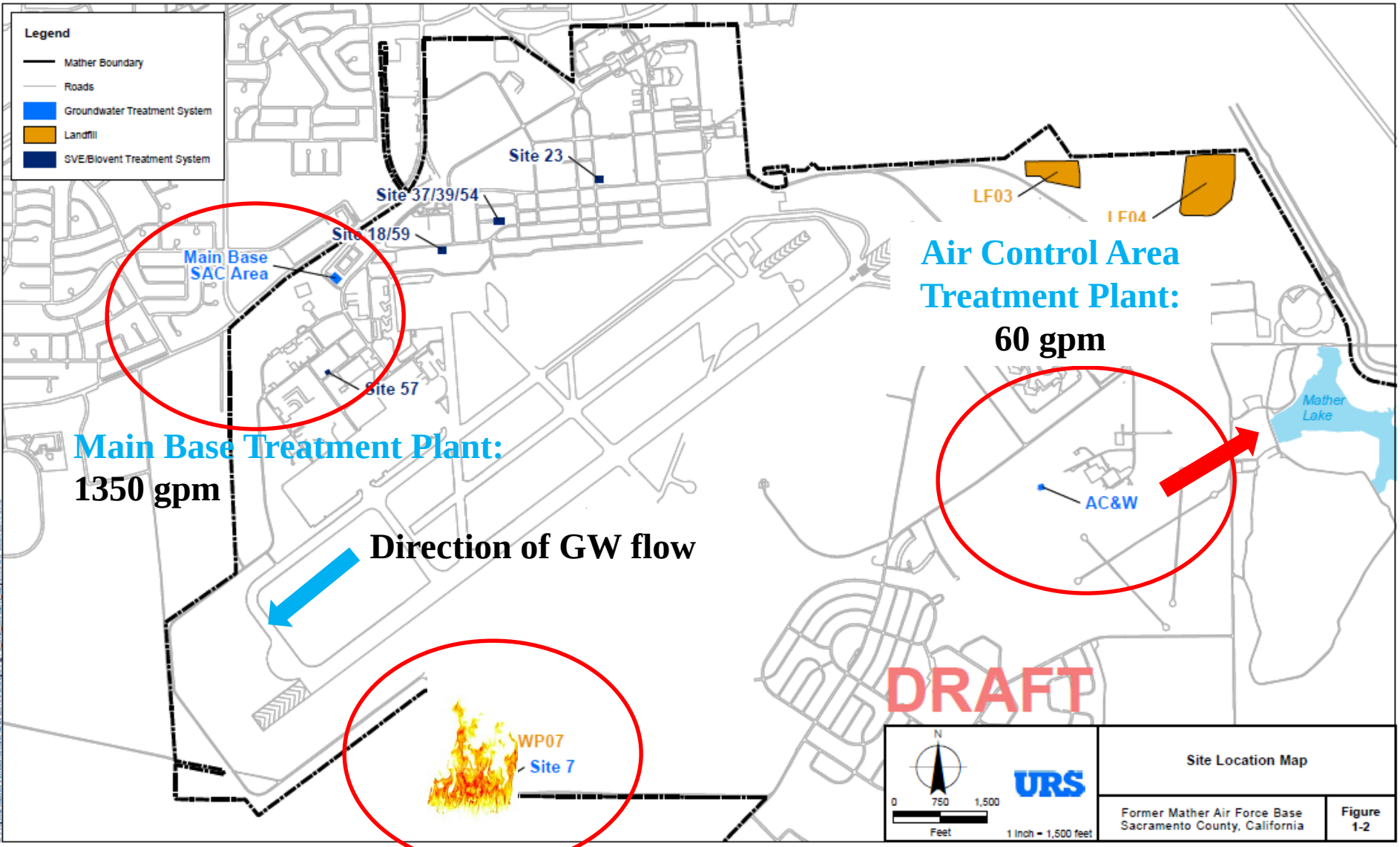


AFFF Partitioning Schematic

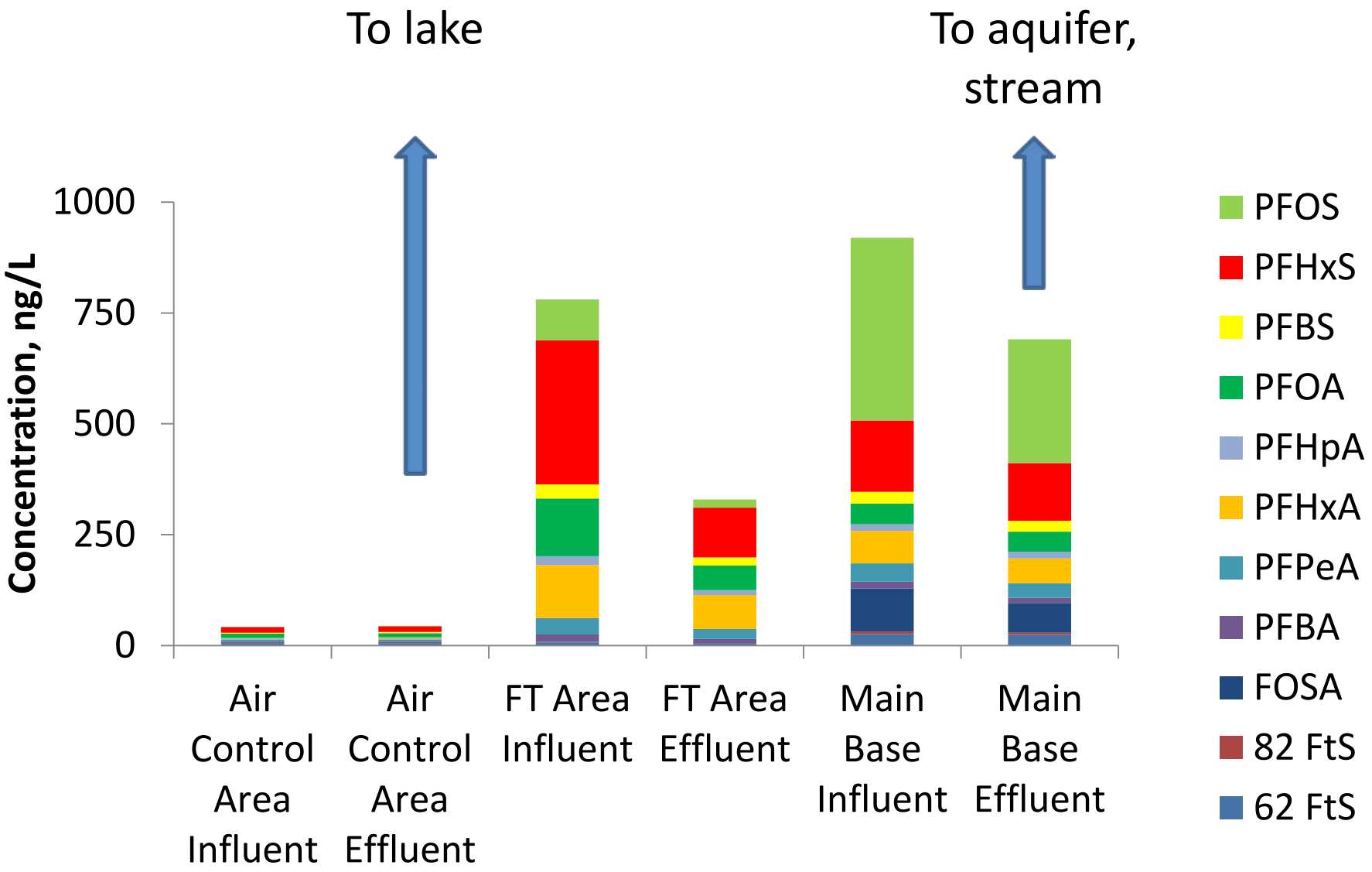


Mather Air Force Base

- Twelve miles north of downtown Sacramento
- 1958 to 1984: Active fire training on base
- 1993: Base closed
- 1998: Groundwater treatment plants installed
- August 2014: Sampling of influent and effluent of three groundwater treatment plants on base for PFASs
  - Treatment consists of air stripping
  - Effluent from one plant goes to a lake at Mather
  - Effluent from another plant gets recharged into an aquifer or to a nearby stream

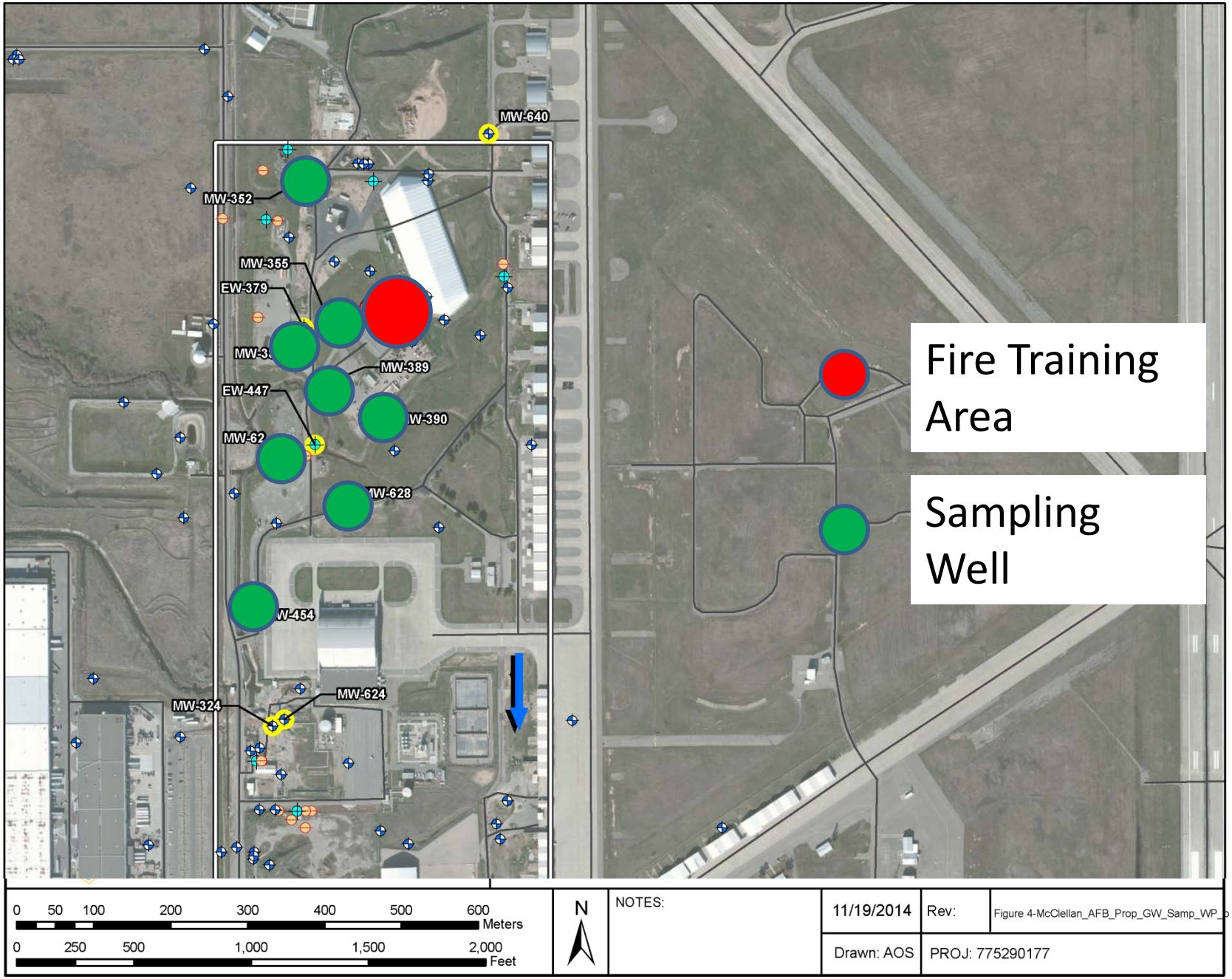


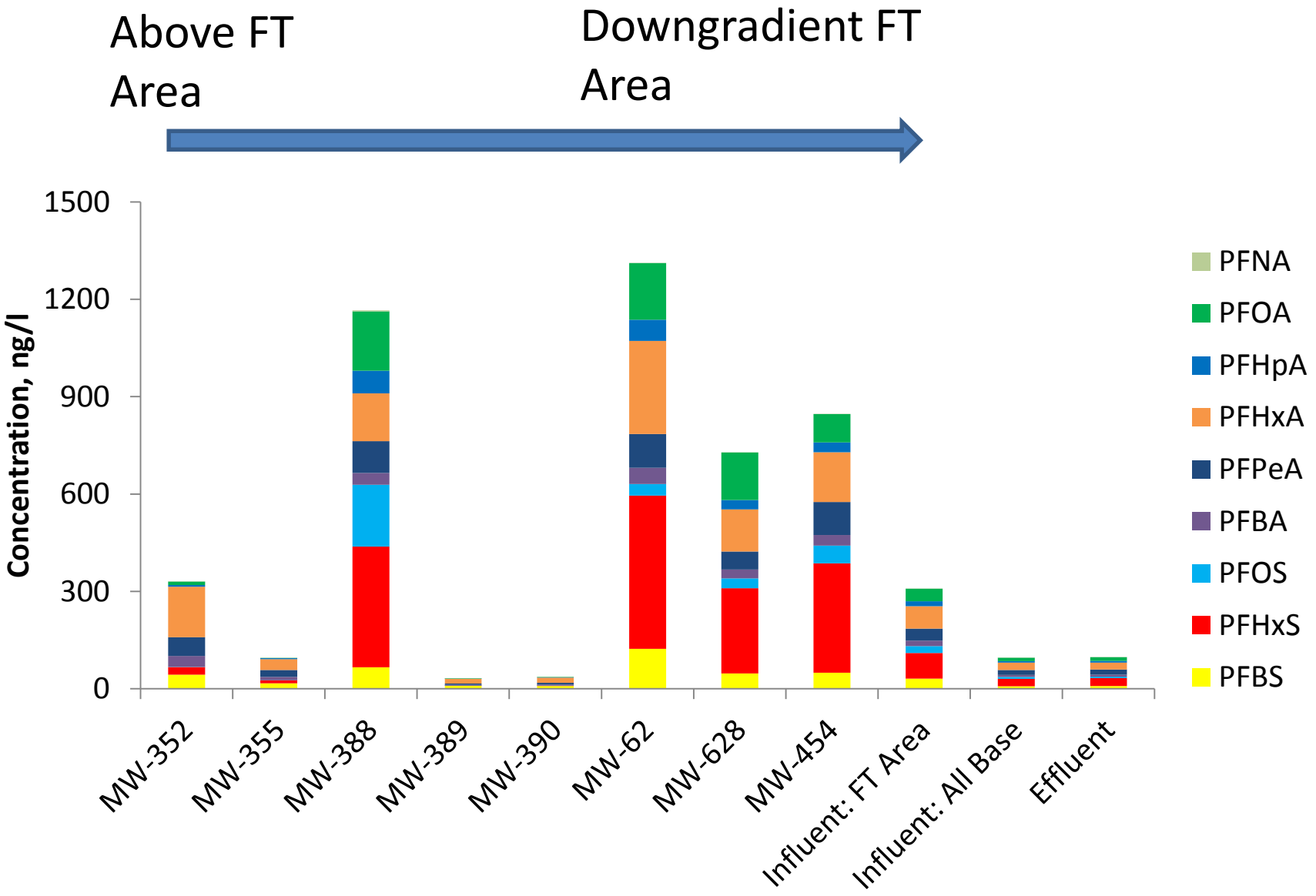
Fire Training Area Treatment Plant:
50 gpm


To lake
To aquifer, stream
Concentration, ng/L
1000
750
500
250
0
Air Control Area Influent
Air Control Area Effluent
FT Area Influent
FT Area Effluent
Main Base Influent
Main Base Effluent
PFOS
PFHxS
PFBS
PFOA
PFHpA
PFHxA
PFPeA
PFBA
FOSA
82 FtS
62 FtS

McClellan Air Force Base

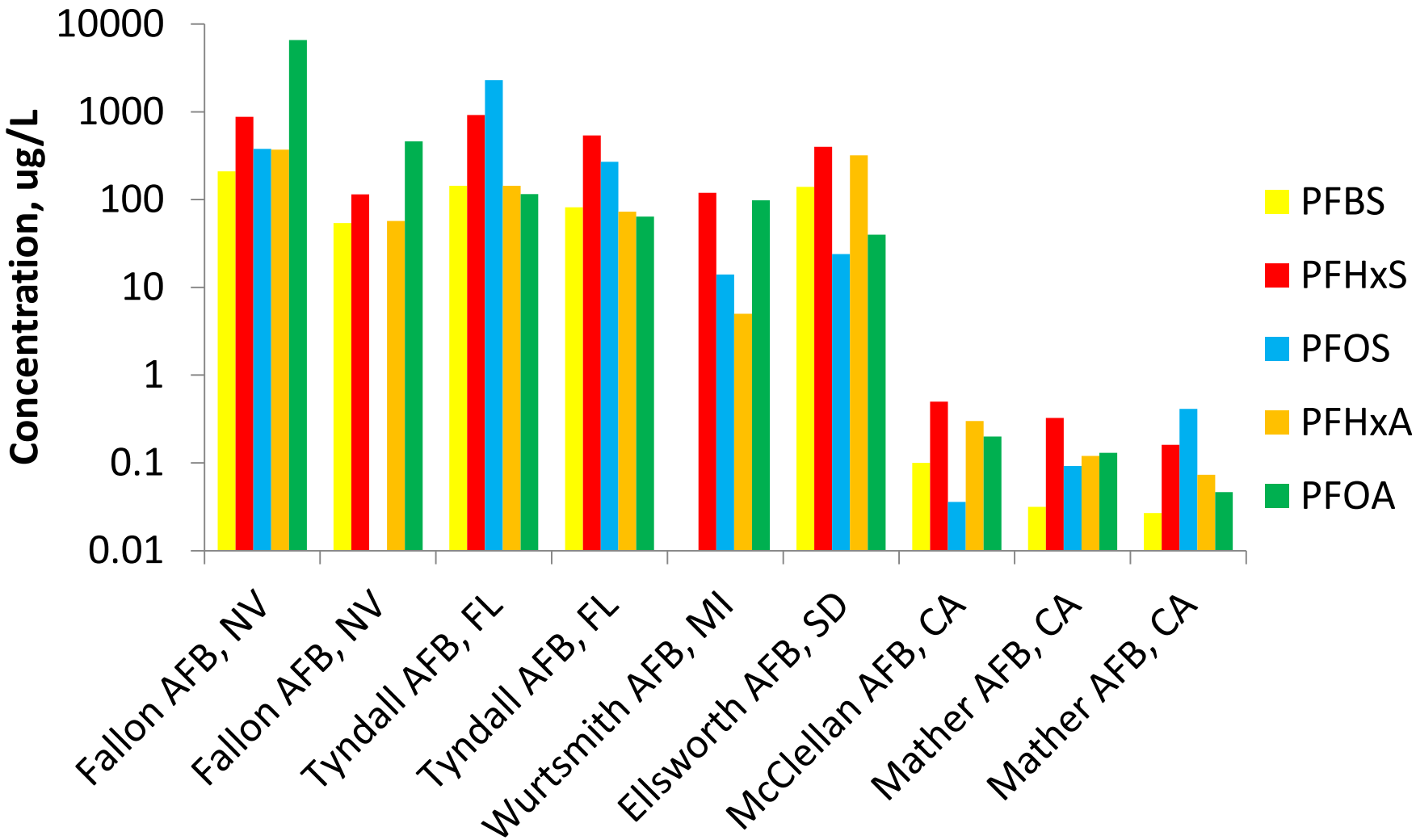
- Seven miles north of downtown Sacramento
- 1977 to 1987: Active fire training on base
  - Petroleum fuels and solvents used for ignition
- 1987: Area capped
- 1993: Cap removed, staining on soil observed
- 1997: Groundwater extraction and treatment
  - Targeting VOCs/SVOCs
- 2001: Base closed
- March 2015: Sampling from GW wells and treatment plant influent/effluent


MW-640
MW-352
MW-355
EW-379
MW-389
EW-447
W-390
MW-62
W-628
W-454
MW-624
MW-324
Fire Training Area
Sampling Well
0 50 100 200 300 400 500 600 Meters
0 250 500 1,000 1,500 2,000 Feet
N
NOTES:
11/19/2014
Rev:
Figure 4-McClellan_AFB_Prop_GW_Samp_WP_
Drawn: AOS
PROJ: 775290177



*No polyfluorinated compounds were detected

Highest [PFASs] at AFB Fire Training Areas



Fallon, Tyndall, Wurstmith data: Schultz et al., *ES&T*, 2004
Ellsworth data: Houtz et al., *ES&T,* 2013

Conclusions for Mather and McClellan

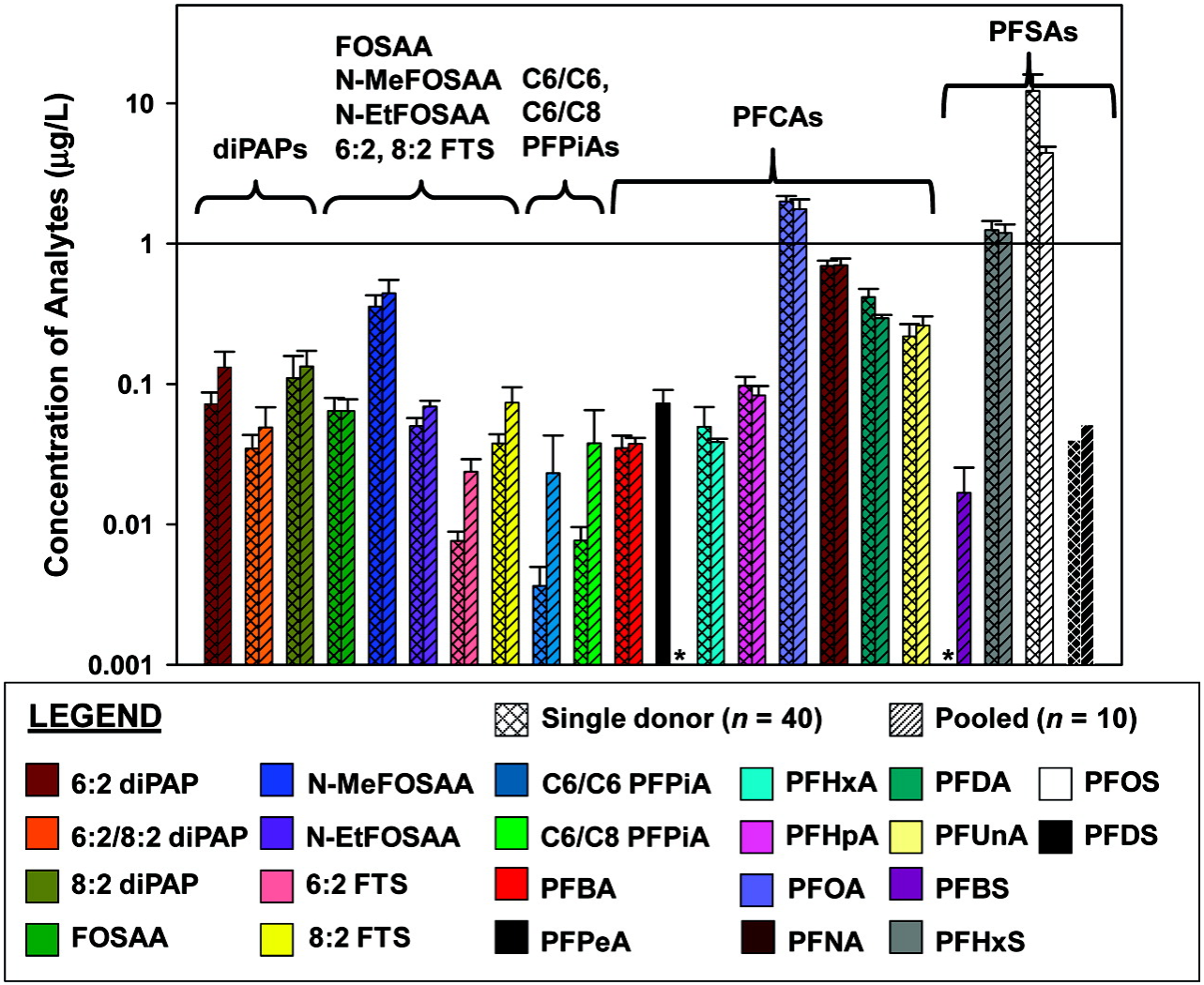
- The two bases have relatively different PFAS profiles
  - Mather: poly- compound and predominately long chain perfluorinated acids
  - McClellan: no poly- compounds and predominately short chain perfluorinated acids
- Mather has relatively highly contaminated groundwater compared to McClellan
- PFAS contamination at both bases lower than seen elsewhere but…
- Mather has some unexpectedly high concentrations discharged to an aquifer and surface water

Implications for CA Biomonitoring

- Short-chain perfluorinated acids are prominent in wastewater and groundwater
  - Short-chain perfluorinated carboxylates (PFBA, PFPeA, PFHxA) not currently included in regular serum PFAS analysis, but difficult to add
  - However, short-chain compounds have much lower bioaccumulation potential

- The only polyfluorinated compounds routinely detected in wastewater and groundwater are 6:2 and 8:2 fluorotelomer sulfonate
  - Easy additions to existing serum method

PFASs in U.S. Human Sera Samples (2009)



Lee & Mabury, *ES&T,* 2011

Implications for CA Biomonitoring

- Indirect analysis of polyfluorinated compounds in wastewater suggest there are relatively high concentrations of unidentified polyfluorinated compounds
  - Direct analysis of more compounds
  - Non-targeted analysis
  - Indirect analysis of polyfluorinated compounds in serum and plasma

PFAS Measurement in Serum

Formic Acid/Online-SPE/4000 QQQ	Methanol Protein Crash and ENVI-CARB cleanup/ 5500 QQQ
Human sample prep time: 1-2 hours, 20 samples + QCs	Human sample prep time: 6-8 hours, 20 samples + QCs
30 minute run times	10 minute run times
Can measure many PFAS analytes of interest but not short chain	Can measure all PFAS analytes of interest (including PFBA, PFPeA)
100% of sample injected	<5% of sample injected
Method LOQs: 10-80 μg/mL, 100 μL serum	Method LOQs:10-100 μg/mL (250 μL serum sample)

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