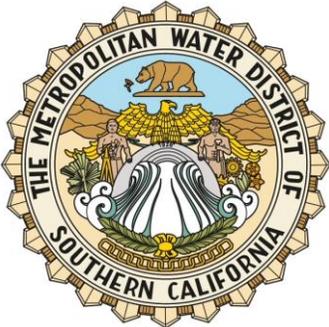


Thank you to our Patrons



We will begin our presentation in a few minutes...



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<https://www.ocwd.com/what-we-do/water-quality/pfas/>



OCWD PFAS Treatment Study

Manmeet “Meeta” Pannu

March 23, 2022

Co-authors: Megan Plumlee, Christine Pham, Mike Hwang, Scott Grieco

Outline



- Introduction to OCWD and PFAS impact
- Study objectives
- Pilot test
- Lab-scale test
- Construction of treatment systems
- Phase II and III testing of adsorbents
- Related research underway

Acknowledgements

- OCWD R&D Dept team →
- OCWD Water Quality and Laboratory Departments
- Jacobs and Battelle
- Media providers for testing included:



What Are PFAS?

- PFAS = Per- and Polyfluoroalkyl Substances
(family of 1000s of man-made chemicals)
- Composed of multiple C-F bonds
- Often labelled as forever chemicals
- Resistant to degradation

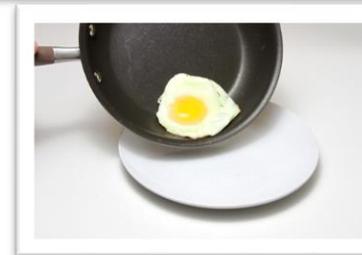
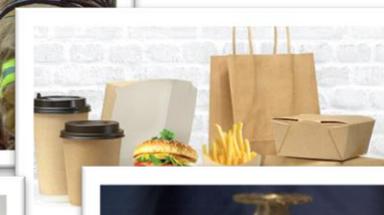
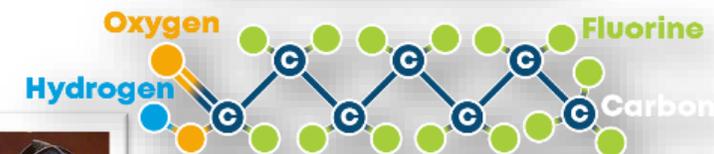
Most common PFAS

PFOA = Perfluorooctanoic Acid ($C_8HF_{15}O_2$)

PFOS = Perfluorooctane Sulfonate ($C_8HF_{17}O_3S$)

PFBS = Perfluorobutanesulfonic acid ($C_4HF_9O_3S$)

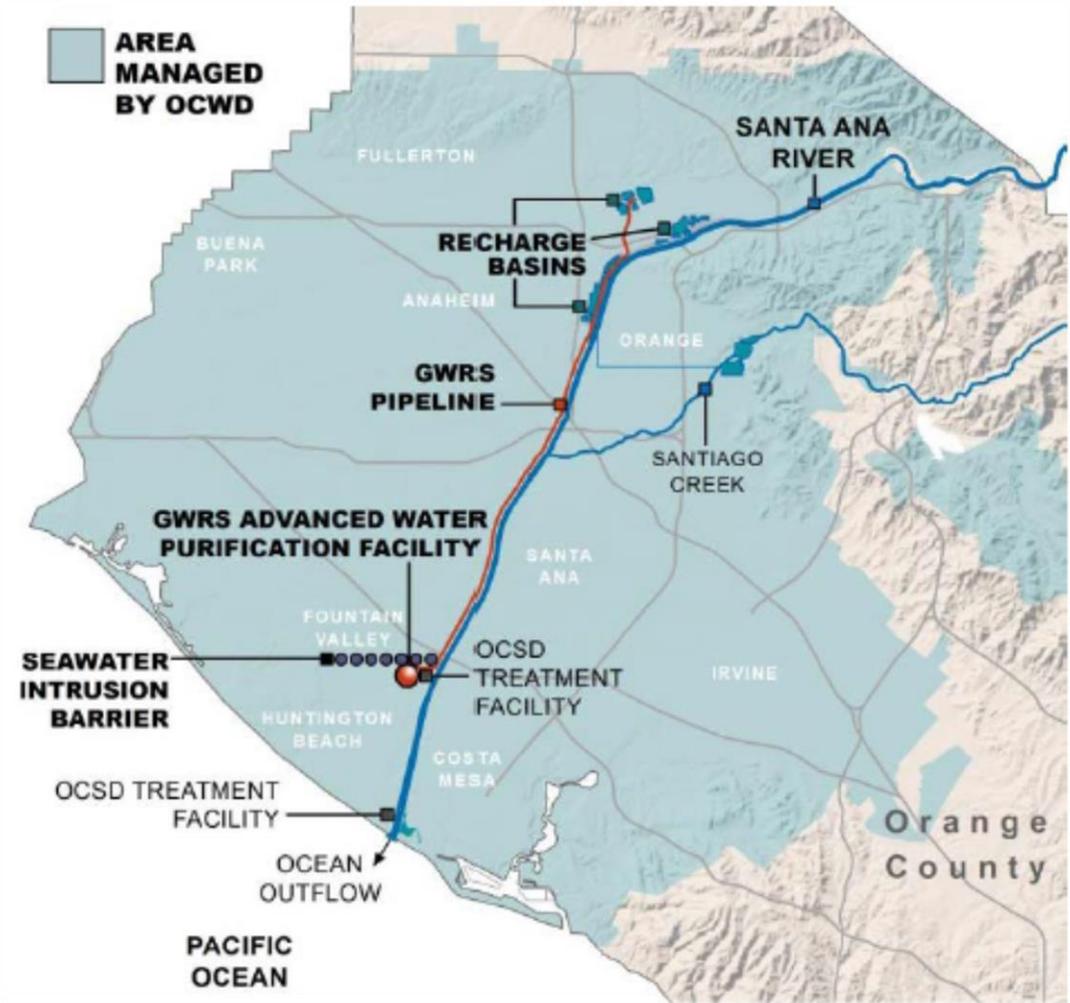
PFAS



Orange County Water District



- OCWD was formed in 1933 to
 - Manage the OC Groundwater Basin
 - Protect rights to Santa Ana River water
- Basin provides groundwater to
 - 19 municipal and special water districts
 - 2.5 million residents
- Basin provides 77% of the water supply for north & central OC



Extent of PFAS Impact in OCWD Service Area



Current California DDW NL/RLs:

Notification Levels (NLs):

PFOA = 5.1 ng/L

PFOS = 6.5 ng/L

PFBS = 500 ng/L

Response Levels (RLs):

PFOA = 10 ng/L

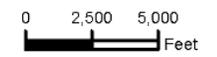
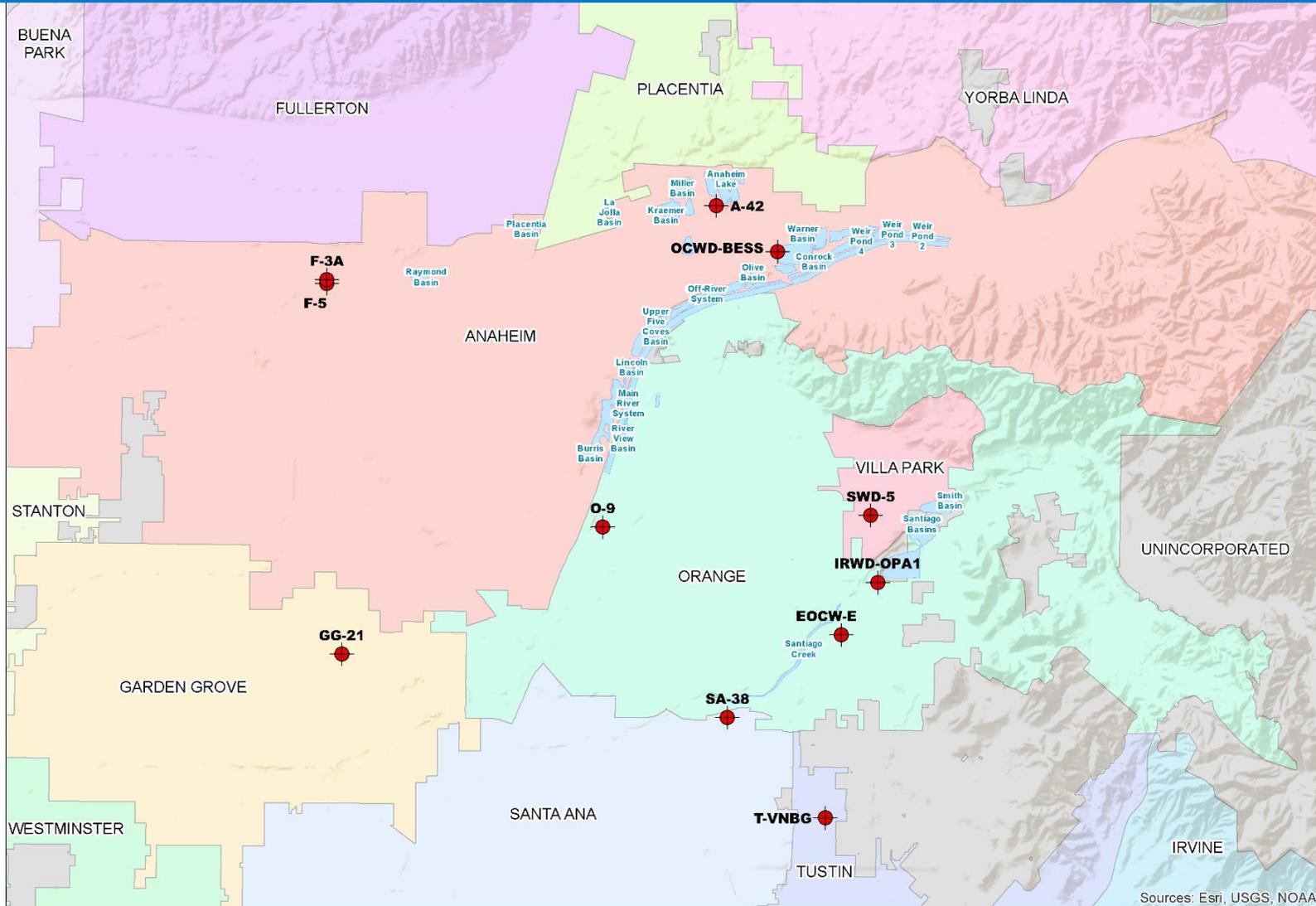
PFOS = 40 ng/L

PFBS = 5,000 ng/L

*Public Health Goal (PHG) process has begun, as required initial step to develop Maximum Contaminant Level (MCL)

- **11 water retailers** (i.e., groundwater “Producers”) in the OCWD service area impacted by 10 ng/L PFOA RL
- **Up to ~ 1/3 of groundwater basin** production (100,000 afy) unable to be served
- **Closure of wells and ~ >\$50 million/year** treated *imported* surface water
- **Solution** is to find an adsorbent based technology to remove PFAS and bring local groundwater supplies back online

Wells Impacted by PFAS Regulations



Sources: Esri, USGS, NOAA

PFAS is not present in advanced treated, recycled water from OCWD's GWRS



- GWRS generates purified water for groundwater augmentation ('indirect potable reuse' or IPR)
- Removal of PFAS by reverse osmosis (RO) is known to be highly effective

<https://www.ocwd.com/gwrs/>



GWRS - new water you can count on

The GWRS is the world's largest water purification system for indirect potable reuse. The system takes highly treated wastewater that would have previously been discharged into the Pacific Ocean and purifies it using a three-step advanced treatment process consisting of microfiltration, reverse osmosis and ultraviolet light with hydrogen peroxide. The process produces high-quality water that meets or exceeds all state and federal drinking water standards.

OBJECTIVE



Granular Activated Carbon (GAC)



Ion Exchange (IX) Resin



Alternative Adsorbents

- What adsorbent should be used to best remove PFAS, and for best value?
- Treatment Study: Test various products at *pilot* and *lab* scale
- Products tested were GAC, IX and Alternative adsorbents

Adsorbents Tested at Pilot and Lab scale Tests



Pilot Adsorbents	# of Products Tested	Empty Bed Contact Time (EBCT)	Supplier(s)/ Manufacturers	Lab (RSSCT)	Pilot	Regenerable?
GAC	8	10 min	Cabot Norit, Calgon, Evoqua, Jacobi	✓	✓	Yes
IX	4	2 min	Calgon, ECT2, Evoqua, Purolite		✓	No
Alternative Adsorbent	1	5 min	Confidential	✓	✓	Yes
Alternative Adsorbent Surface-modified bentonite (FLUORO-SORB® 200)	1	2 min	CETCO	✓	✓	No

GAC



IX

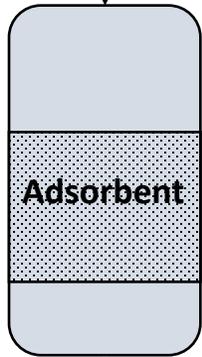
Alternative



How does adsorbent technology work? Breakthrough Curve

Influent water

PFAS

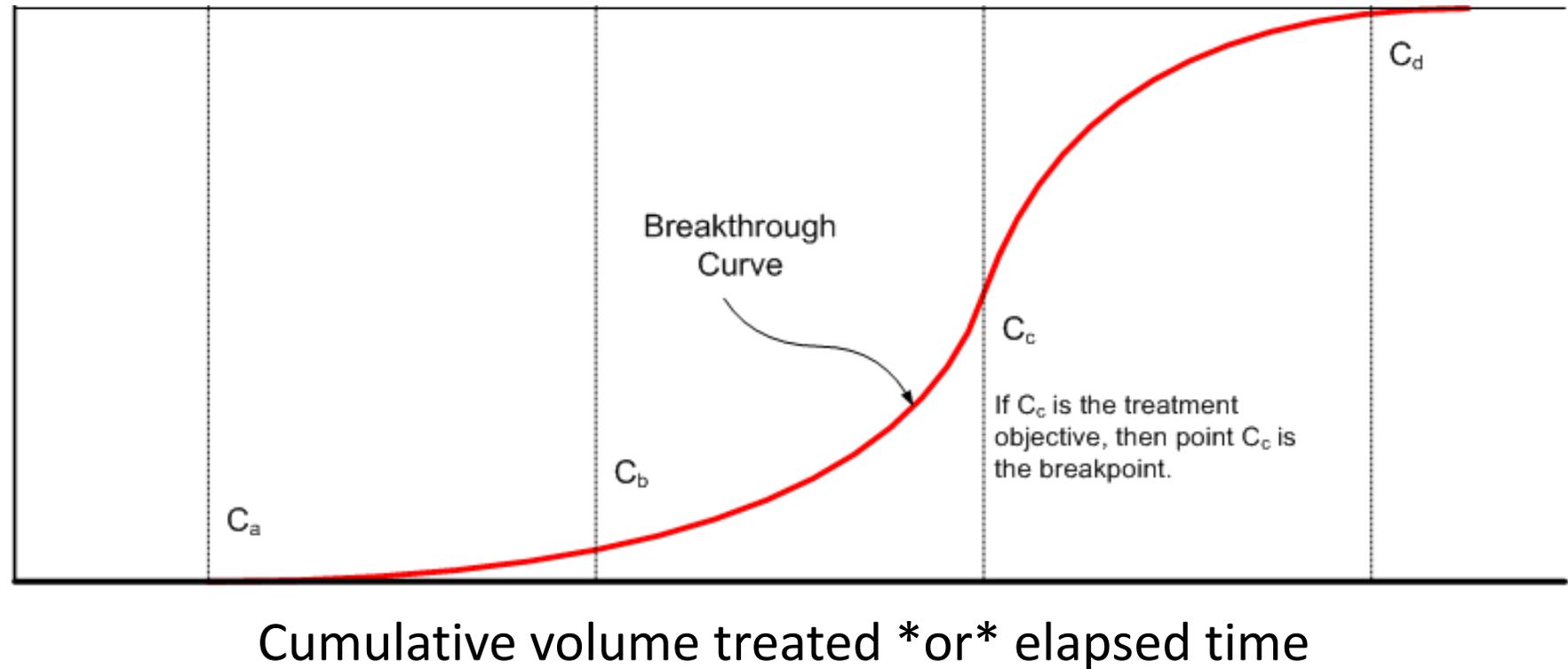


Adsorbent

Effluent water



PFAS (ng/L) in Treated Effluent



OCWD Pilot Program

- Pilot ★ water supplied by OCWD-owned non-potable well in Anaheim
- PFAS in pilot influent:

PFAS (EPA 537.1)	Mean (ng/L)
PFOA (long-chain)	16
PFOS (long-chain)	23
PFHxS (long-chain)	11
PFBS (short-chain)	15
PFHxA (short-chain)	3



OCWD Pilot Program



Installed pre-fab building to house pilot

Pilot Skids

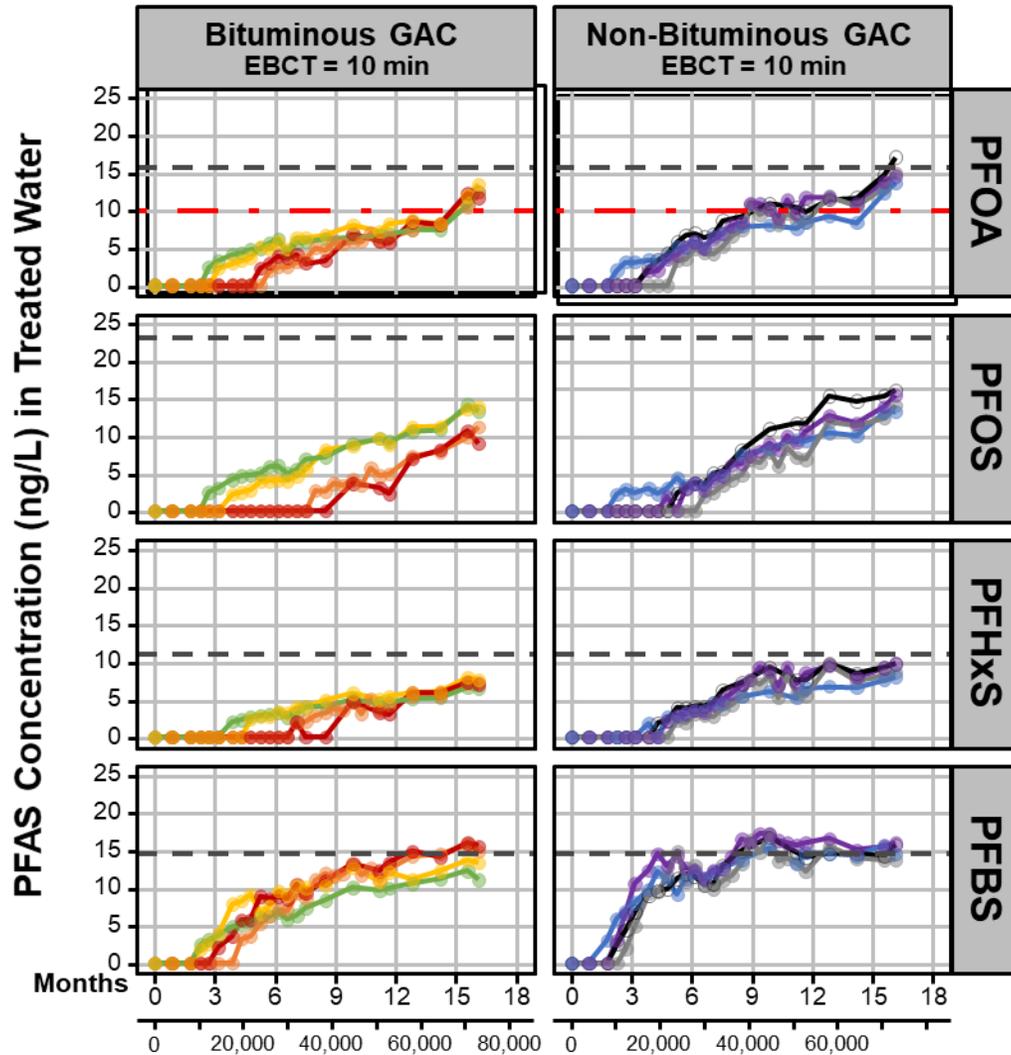
Ion Exchange (IX) pilot skid (1 skid x 6-column)

[0.9 m or 3 ft height]



Granular activated carbon (GAC) pilot skids (2 skids x 4-column [1.5 m or 5 ft height])

GAC Performance Pilot Results



- GACs:** Bituminous GACs (e.g., Calgon F400) performed better than non-bituminous or blended products. Overall, Calgon F400 superior performance (taking into account PFOA + PFOS).

- - - Average Influent Concentration
 - - - CA DDW PFOA Response Level = 10 ng/L

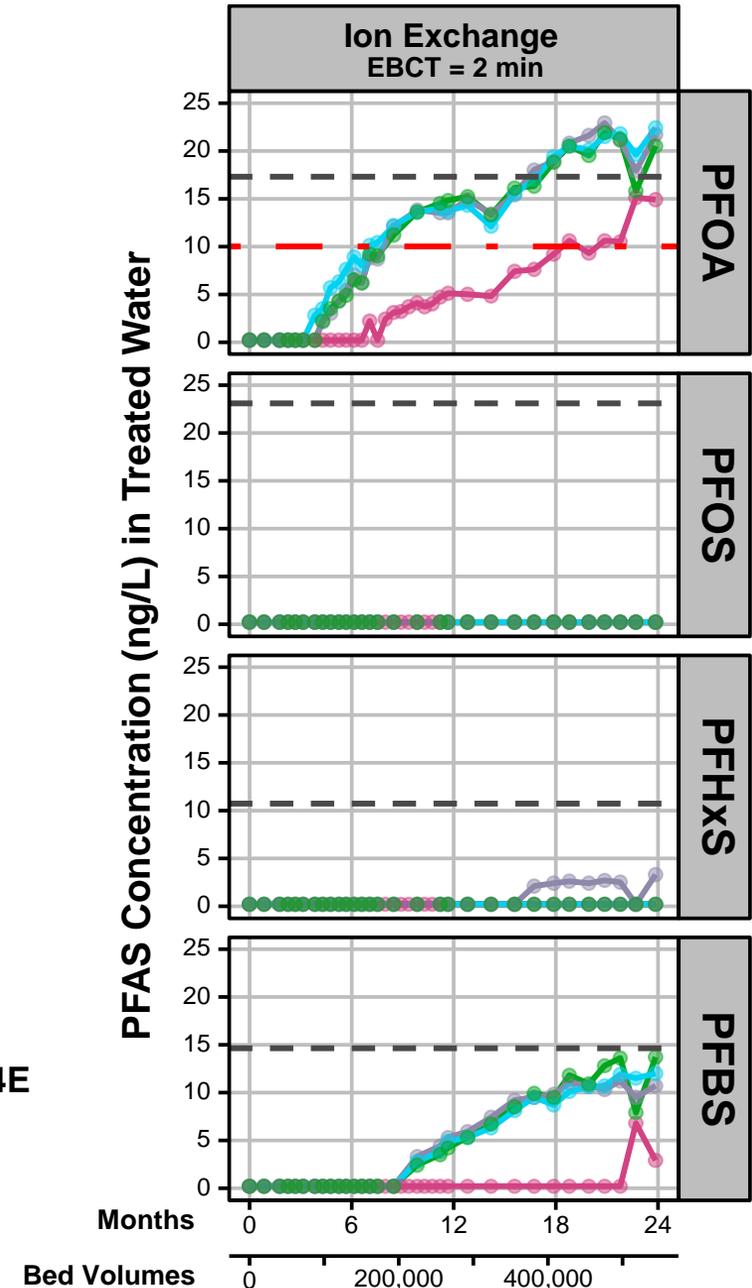
- Cabot Norit GAC400
- Calgon F400V (Virgin)
- Calgon F400R (Reactivated)
- Calgon F600
- Evoqua UltraCarb 1240LD
- Evoqua AquaCarb 1230CX
- Cabot Norit HYDRODARCO 4000
- Jacobi AquaSorb F23

IX Performance Pilot Results

- Evoqua PSR2+ showed superior performance (later PFOA breakthrough) relative to other IXs for OCWD pilot
 - *Disclaimer: Adsorbent performance may be quite site-specific* (IX, GAC, AA), thus our findings may be different than other utilities (general need for site-specific performance testing)*
- All 4 IXs showed later breakthrough of short-chain PFAS (PFBS), and sulfonates (PFOS, PFHxS) relative to all 8 GACs (shown on previous chart)

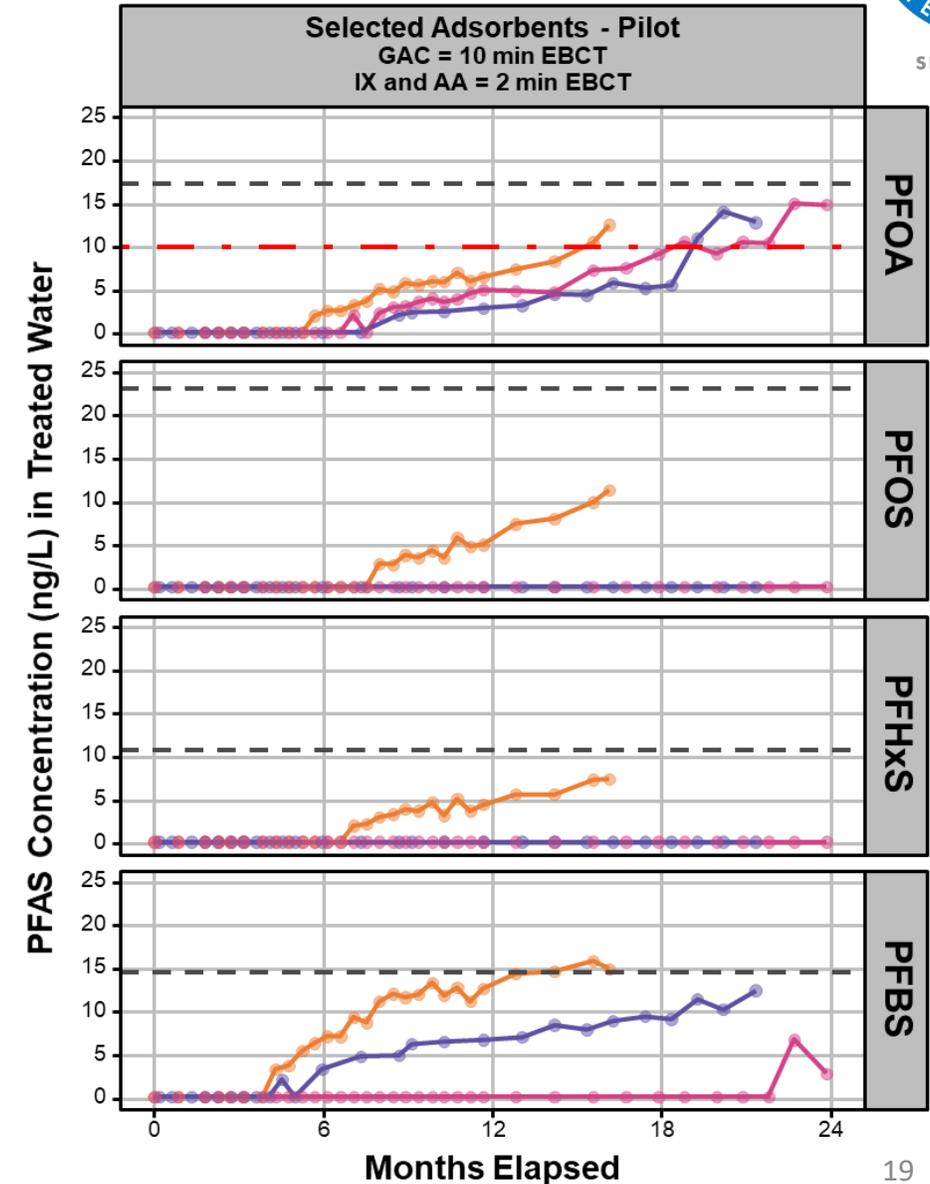
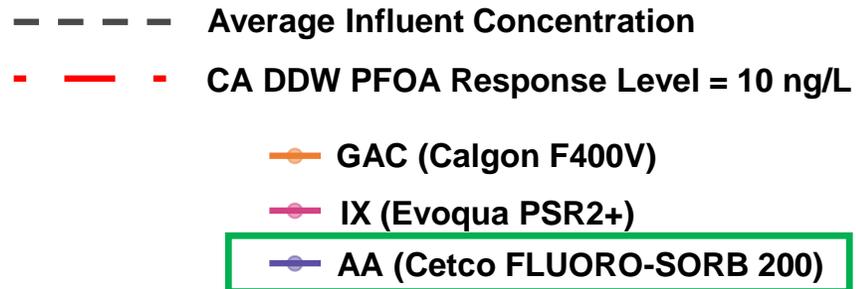
- - - Average Influent Concentration
 - - - CA DDW PFOA Response Level = 10 ng/L

- Purolite Purofine PFA694E
- Calgon CalRes 2301
- Evoqua PSR2+**
- ECT2 Sorbix LC4



GAC vs IX vs Alt. Adsorbents (AA)

- Encouraging results for alternative adsorbent **CETCO FLUORO-SORB® 200** showing similar performance for PFOA as pilot's **best-performing IX** (at same low-footprint 2-min EBCT!)
- Merits consideration for full-scale treatment
- This AA is new to the drinking water market; OCWD and other water agencies currently reviewing with regulators



Rapid Small Scale Column Testing (RSSCT) in Lab

- RSSCT was performed at bench (lab) scale with GAC and alternative adsorbents
- RSSCT – Advantage (over pilot) is the ability to **quickly** screen **multiple** waters
- Tested water from 9 different producers (production wells in OC) plus OCWD pilot influent water (**10 total waters**)
- RSSCT on CD (constant diffusivity) assumptions
- Only presenting results for PFOA

BATTELLE
Jacobs



0.7 cm diameter
1.0 - 3.4 cm bed depth

Drum Filling from different producers' for RSSCT Testing

ORANGE COUNTY WATER DISTRICT
09/10/2019
GROUNDWATER (OCWD-BESS-1)
PFAS PILOT WELL TESTING

1811/11 01/10/19
USA 711 4602

1811/11 01/10/19
USA 711 4602
WITH VENTED GASKETS

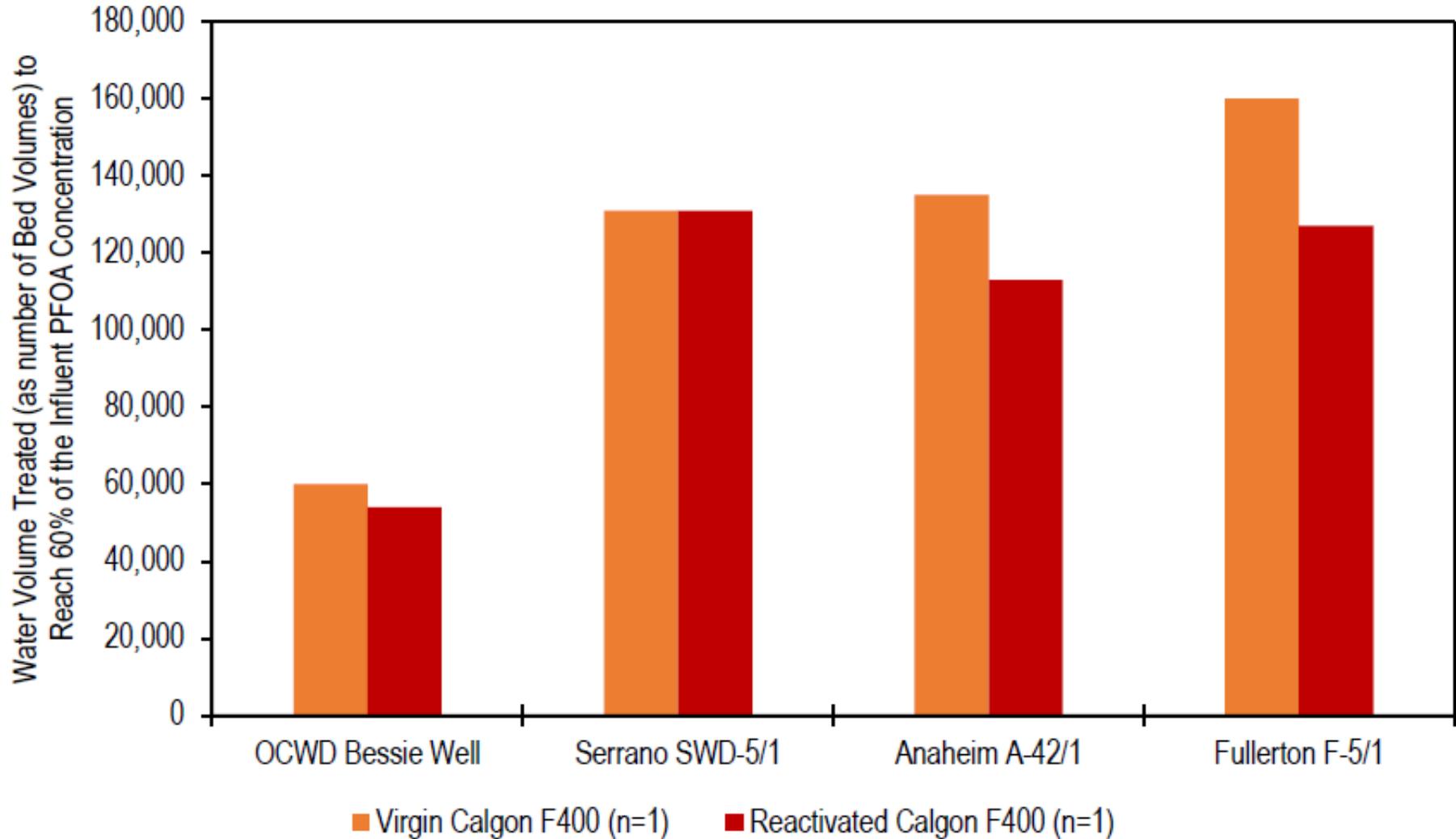


RSSCT– Lab Testing



LAB (Battelle, Ohio)

Calgon F400: Virgin & Reactivated

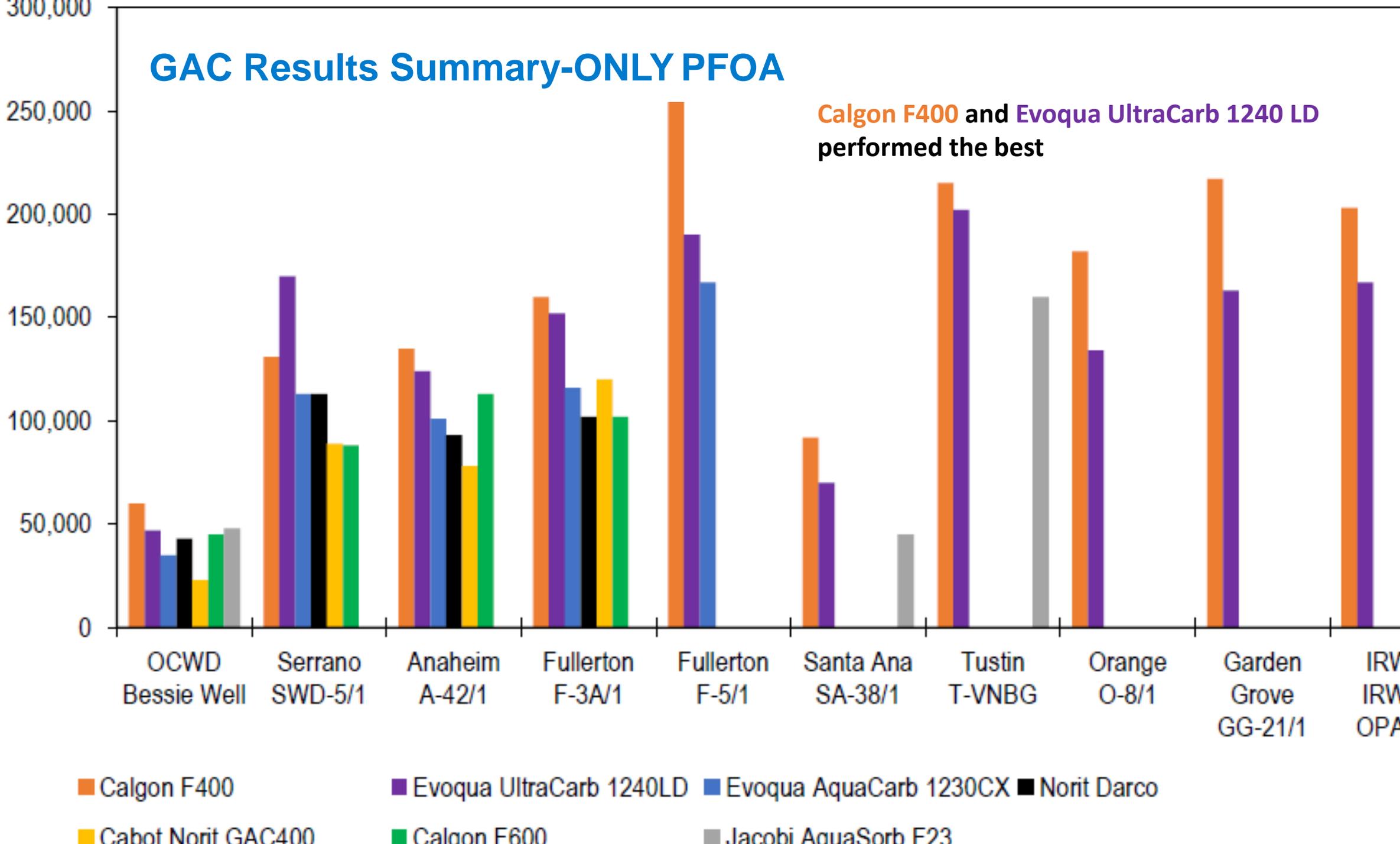


- Virgin GAC may provide longer life with lower DOC
- GAC performance varied by the water producer/water quality

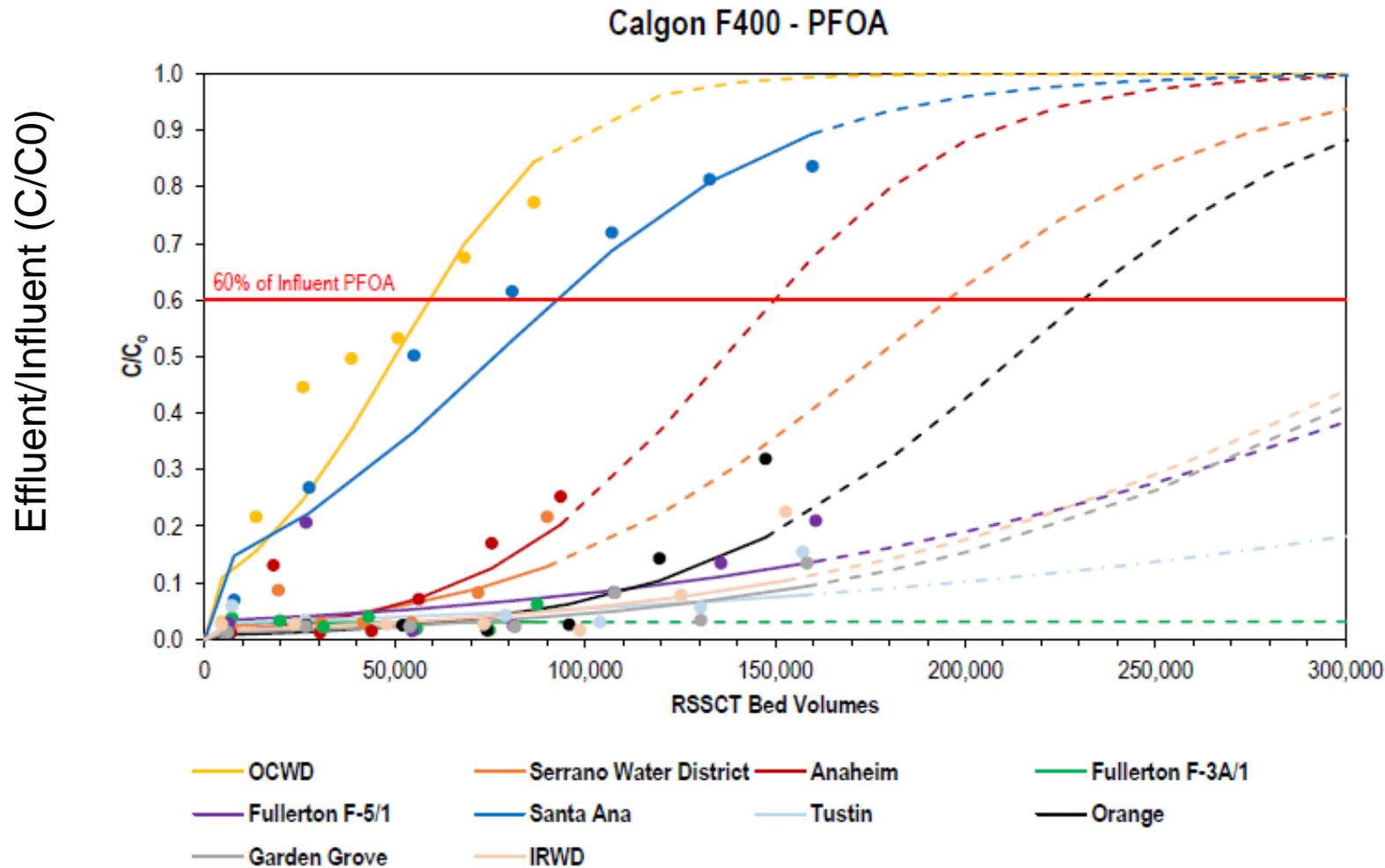
Bed volumes to reach 60% of Influent PFOA concentrations

GAC Results Summary-ONLY PFOA

Calgon F400 and Evoqua UltraCarb 1240 LD performed the best



Calgon F400: Producer Differences due to DOC level



- Calgon F400 was the best performing based on our Pilot and Lab tests
- Large dependency of GAC performance on producer water quality (particularly DOC levels)
 - Bessie (OCWD well) had the highest DOC
 - DOC range is 0.2 to 1.6 mg/L

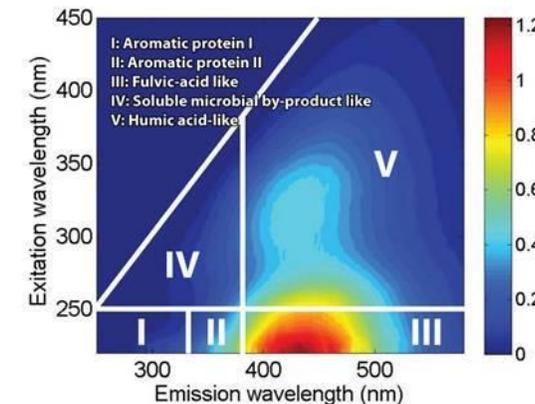
Influence of DOC Character

- Excitation Emission Matrix (EEM) Fluorescence Spectroscopy

Heat Maps

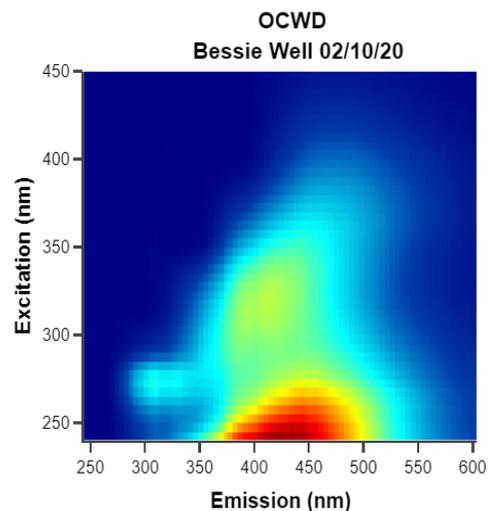
- Five excitation-emission regions:

- Aromatic proteins (I, II)
- Fulvic acids (III)
- Hydrophilic acids (IV)
- Humic acids (V)

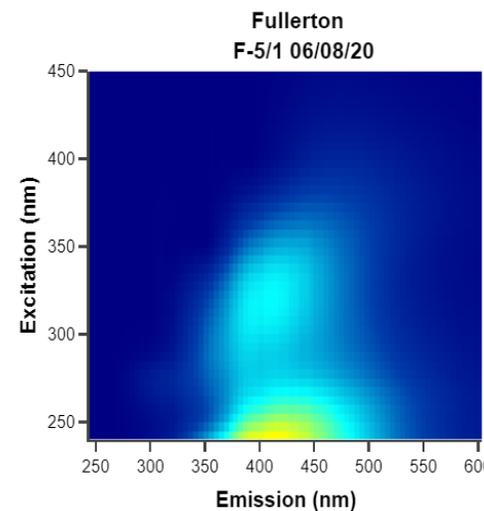


- Provided in fluorescence units (AFU)

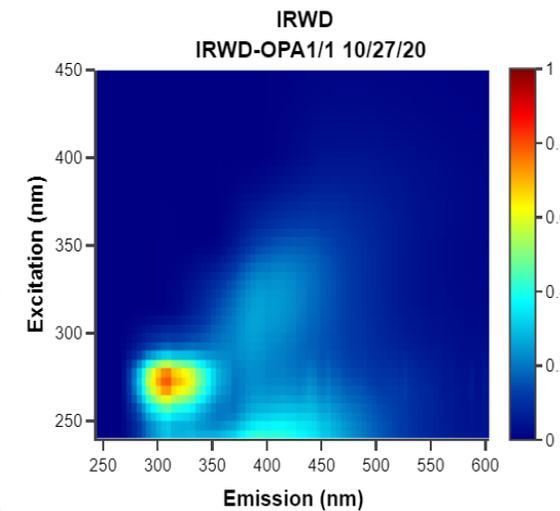
DOC=1.6 mg/L



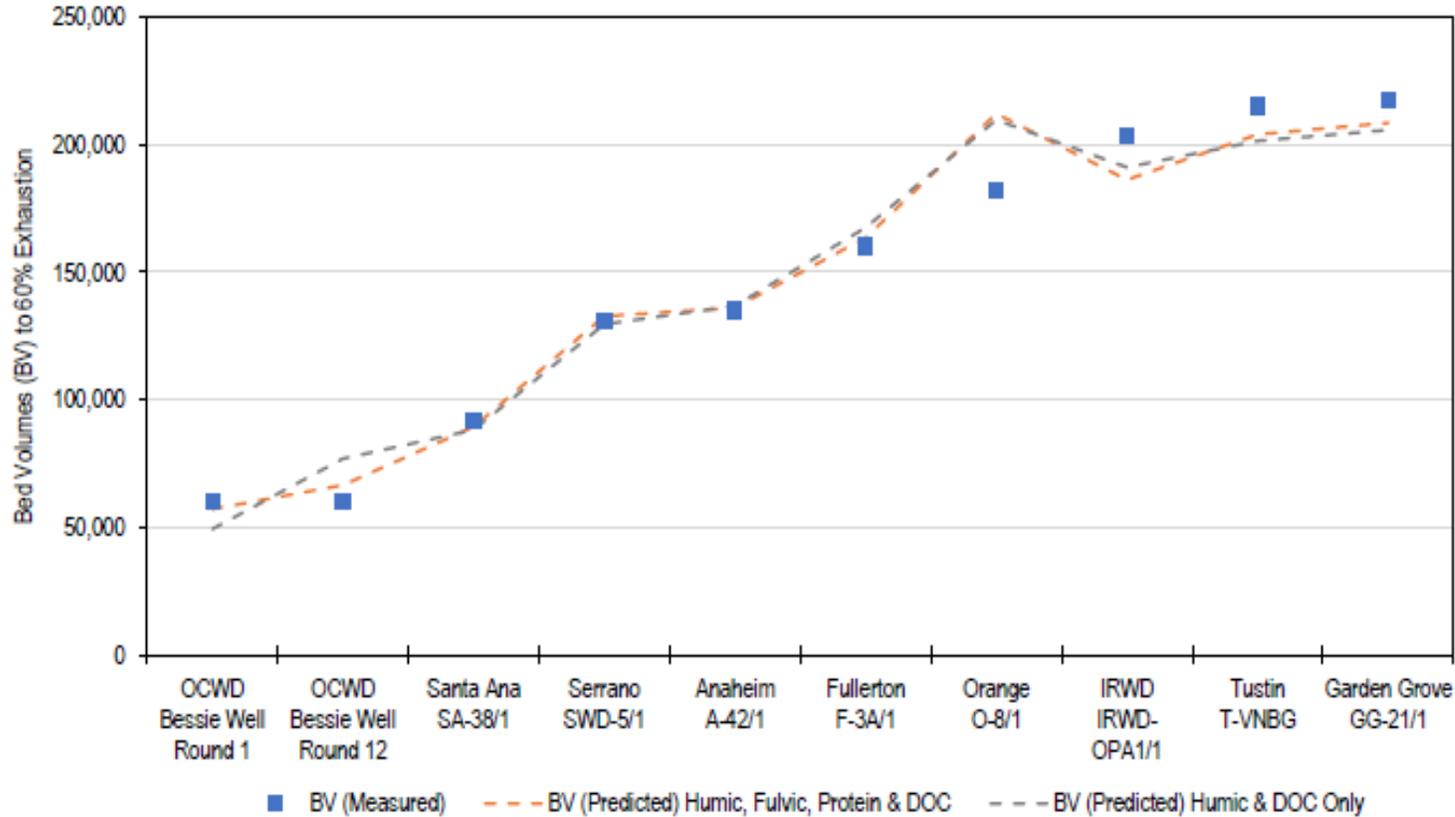
DOC= 1.44 mg/L



DOC= 0.47 mg/L



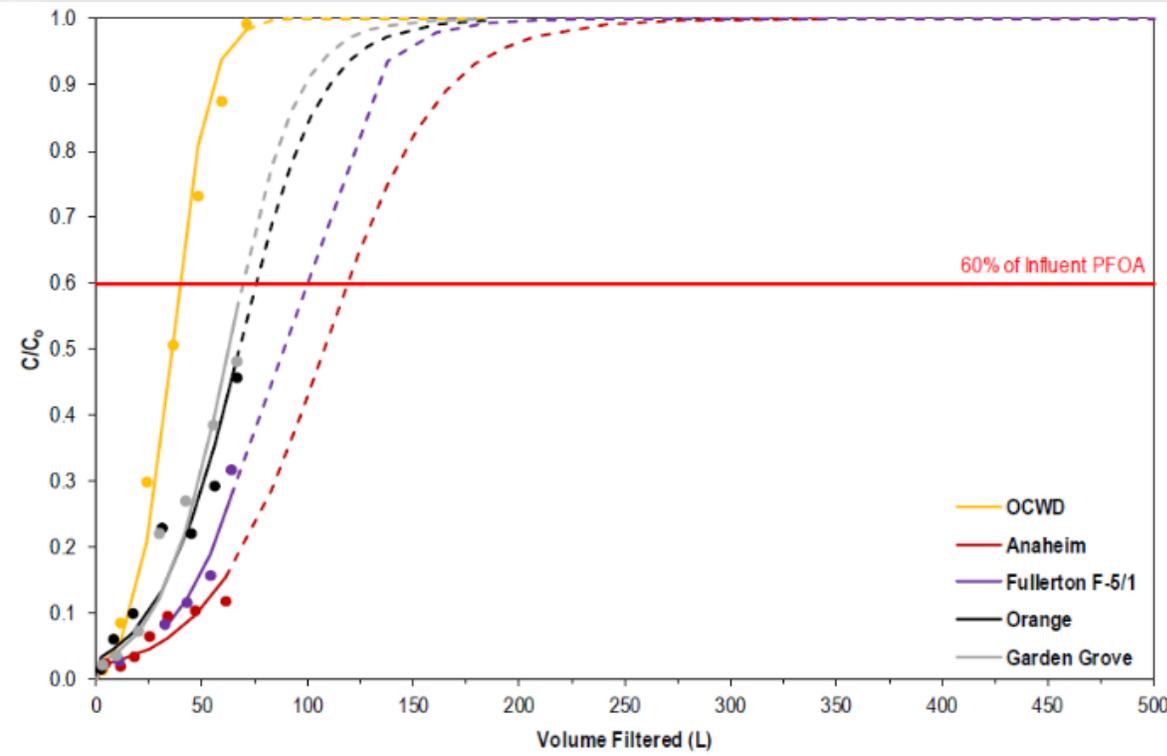
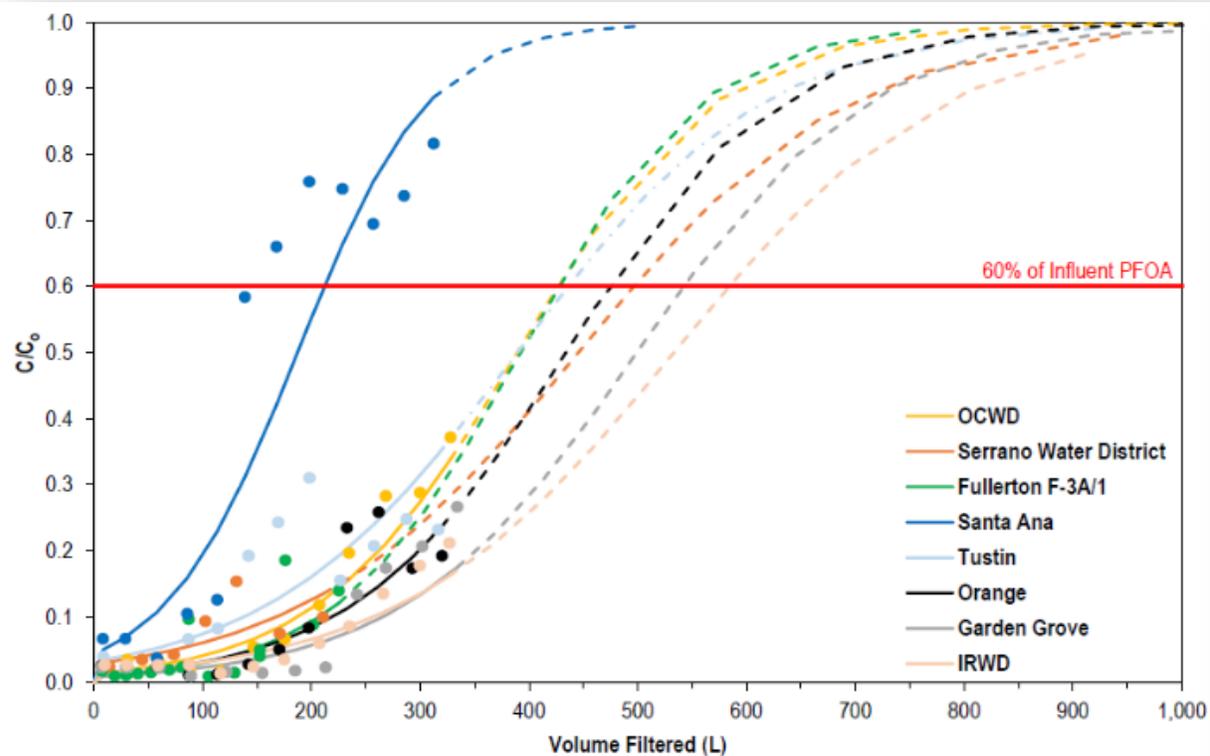
Multi-variable Regression



- Evaluated influence of
 - DOC
 - Humic acids
 - Fulvic acids
 - Aromatic proteins
- DOC and Humic acids were significantly correlated with the data ($p < 0.05$)
- GAC performance can be predicted based on DOC and Humics ONLY

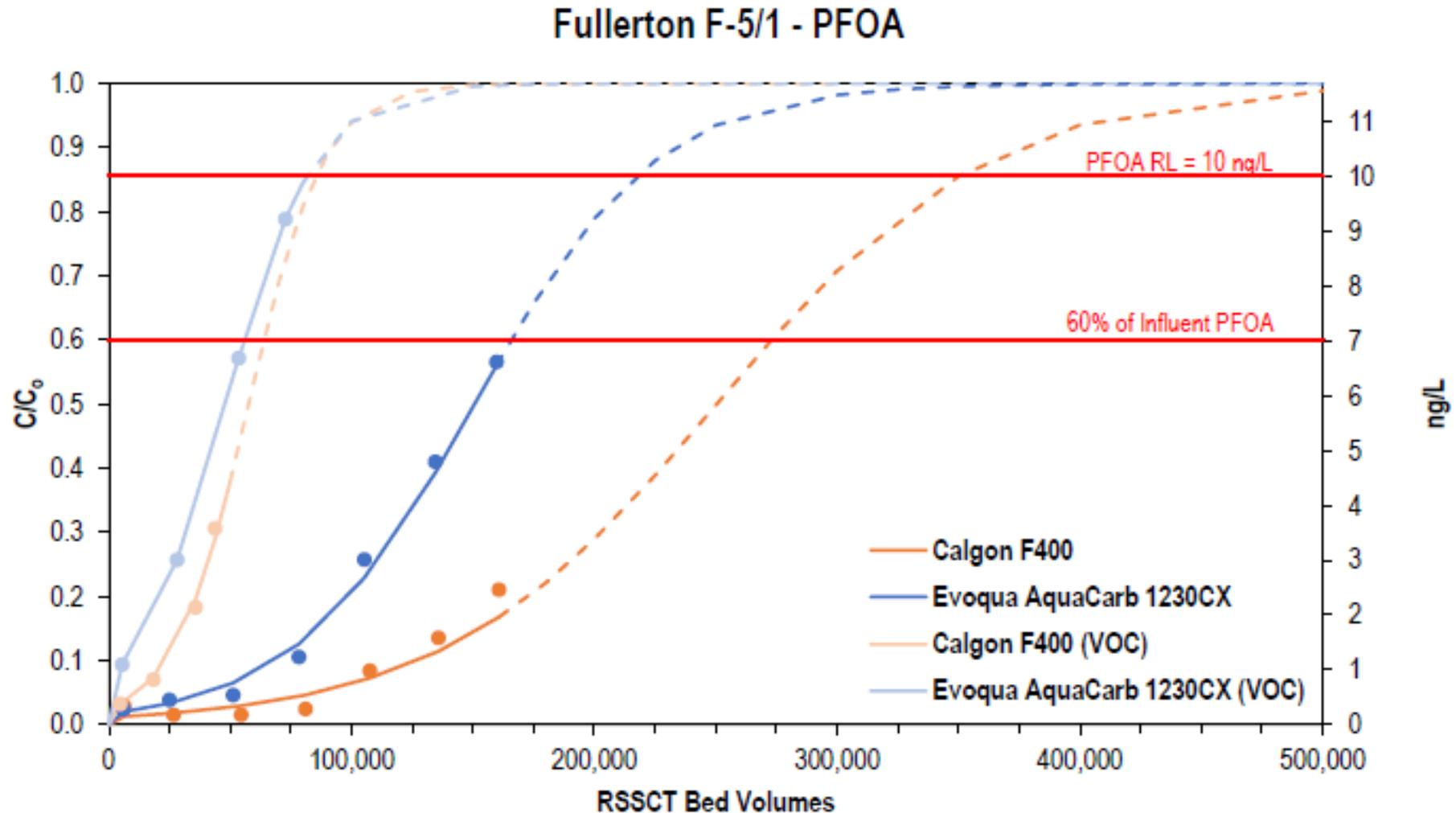
$$BV_{60\%} = 241748 - 9772(HA: AFU) - 69482(DOC: \frac{mg}{L})$$

Alternative Adsorbents (Left; Cetco FS200)

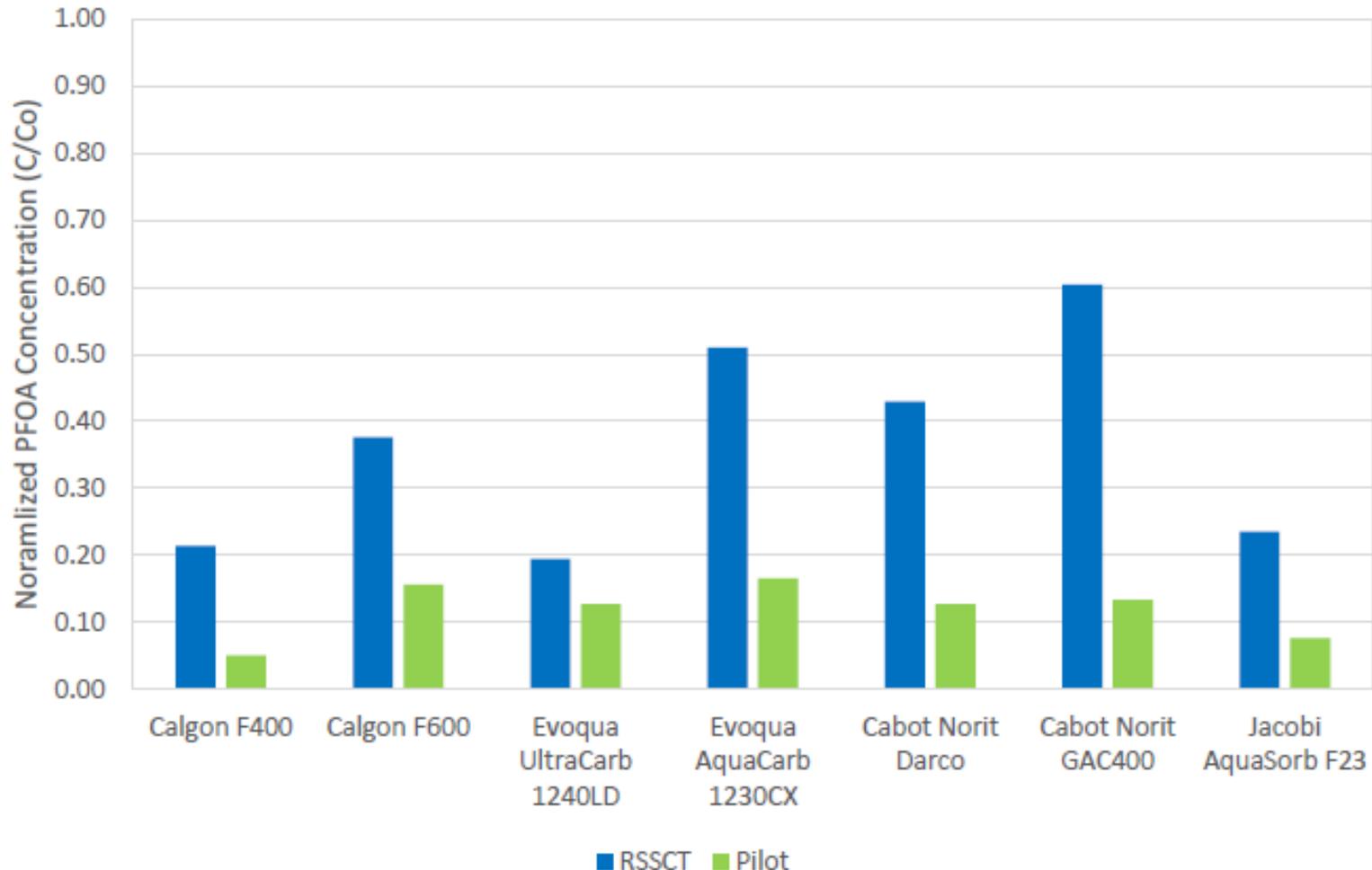


- Fluoro-Sorb 200 performed superior to another alternative adsorbent with later PFOA breakthrough
- Little difference among different producers except Santa Ana
- Alternative adsorbent performance is less impacted by DOC as compared to GAC
- FS200 had same superior results in the pilot

Addition of VOCs



RSSCT to Field-Scale Comparison for GAC

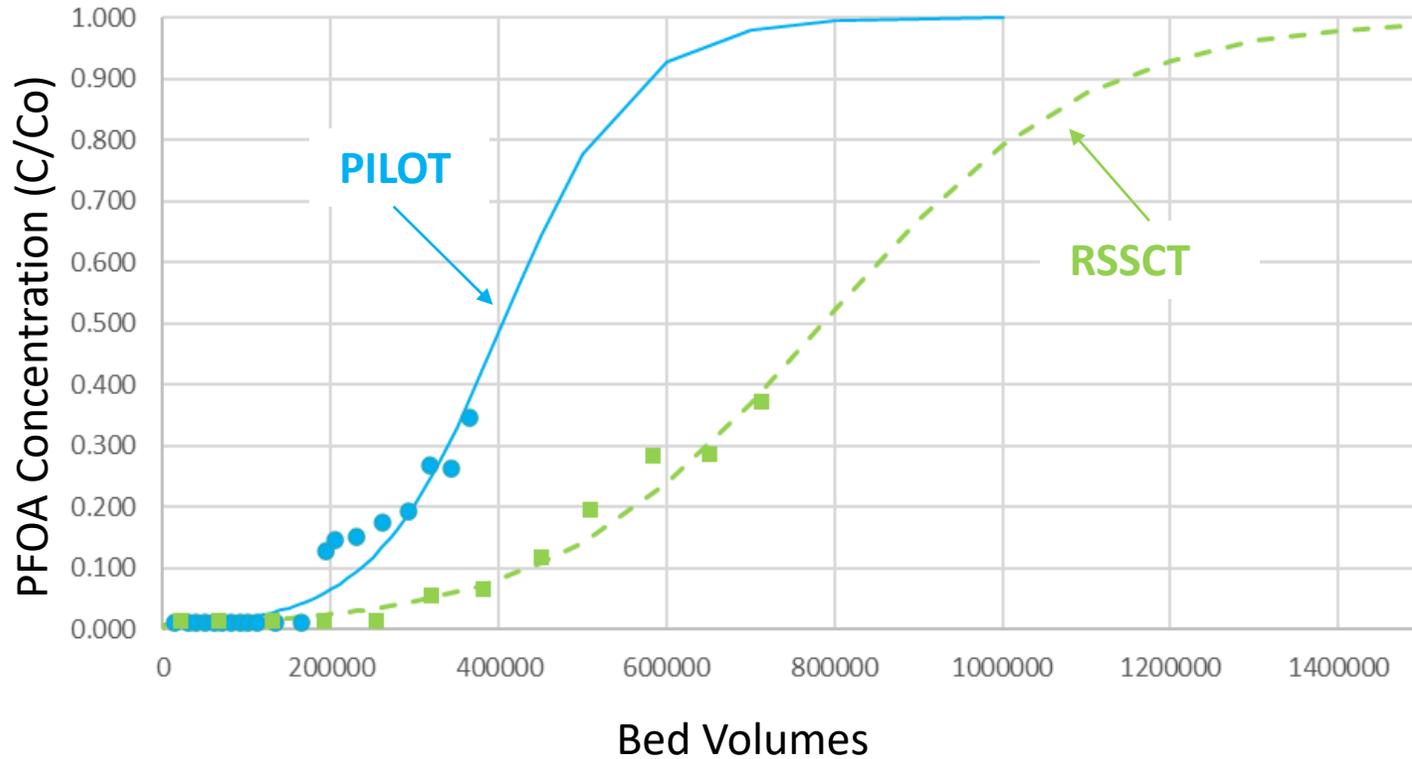


- Systems evaluated at 150 days of operation (~21,600 BV)
- RSSCT exhibits faster breakthrough in every product
 - Conservative when assessing initial breakthrough

RSSCT to Field-Scale Comparison for FLUORO-SORB

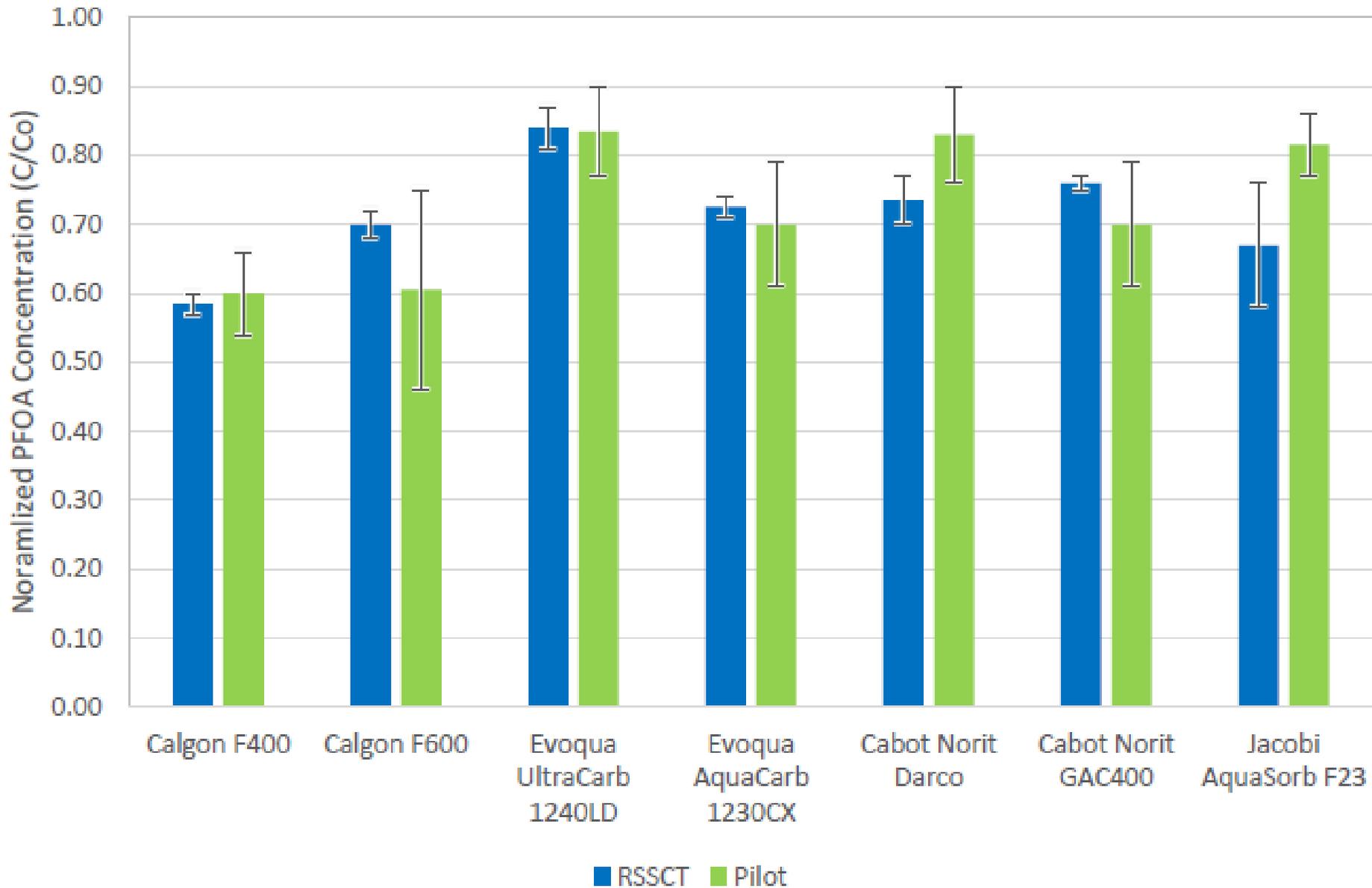


FLUORO-SORB 200



- CETCO FLUORO-SORB 200 RSSCT showed much later PFOA breakthrough than pilot (*not conservative!*)
- RSSCT data predicted ~2x greater runtime than actual from pilot

RSSCT to Field-Scale Comparison (cont.)



- Systems evaluated at 390 days of operation (~56,000 BV)
 - RSSCT predictive of full-scale at typical lead bed changeout exhaustion
 - F600, GAC400 greater C/C_0 for RSSCT
- Within estimated margin of error of testing

Generalized Cost Evaluation

- Costs for the 2 best GACs (Calgon F400 and Evoqua UC1240LD) were similar across sites within ~10%
 - Longer media life for lower DOC water
- Class IV estimates indicate total unit cost (\$/acre-ft) for water treatment (capital + O&M) were GAC > IX >> FS200
- Nanofiltration projected to have the highest total unit water costs compared to all media technologies



Conclusions

- All adsorbents tested can **successfully remove PFAS** to meet California water quality guidelines
- **Bench- and pilot-scale testing useful** to select adsorbents: Certain products had longer life removing PFOA
- Bench-scale testing revealed strong **dependency of GAC life on DOC** concentration and character
- Comparing RSSCT results to pilot-scale **validates the use of RSSCT for GAC** (i.e., predicts PFAS breakthrough fairly well), **but not the alternative adsorbents** where RSSCT predicts significantly later breakthrough of alternative adsorbents

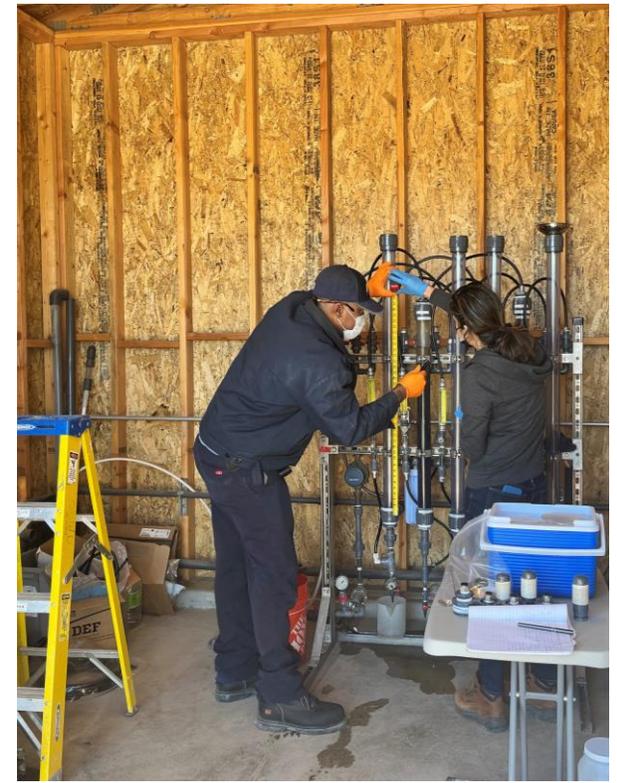


Conclusions (cont.)

- All 4 **IX products showed later breakthrough of sulfonates** (PFOS, PFHxS) **and short-chain PFAS** (PFBS) relative to all 8 GACs
- **Alternative adsorbents:** Encouraging results though varies by product
- While all media removed PFAS from water, performance (i.e., **lifetime** between media change-outs) **varied dramatically**.
- In our study, Class IV estimates (+50%/-30%) indicate total unit water cost (capital + O&M) as GAC > IX >> FS200



What Now?



Phase I- ✓

Phase II and III-Ongoing

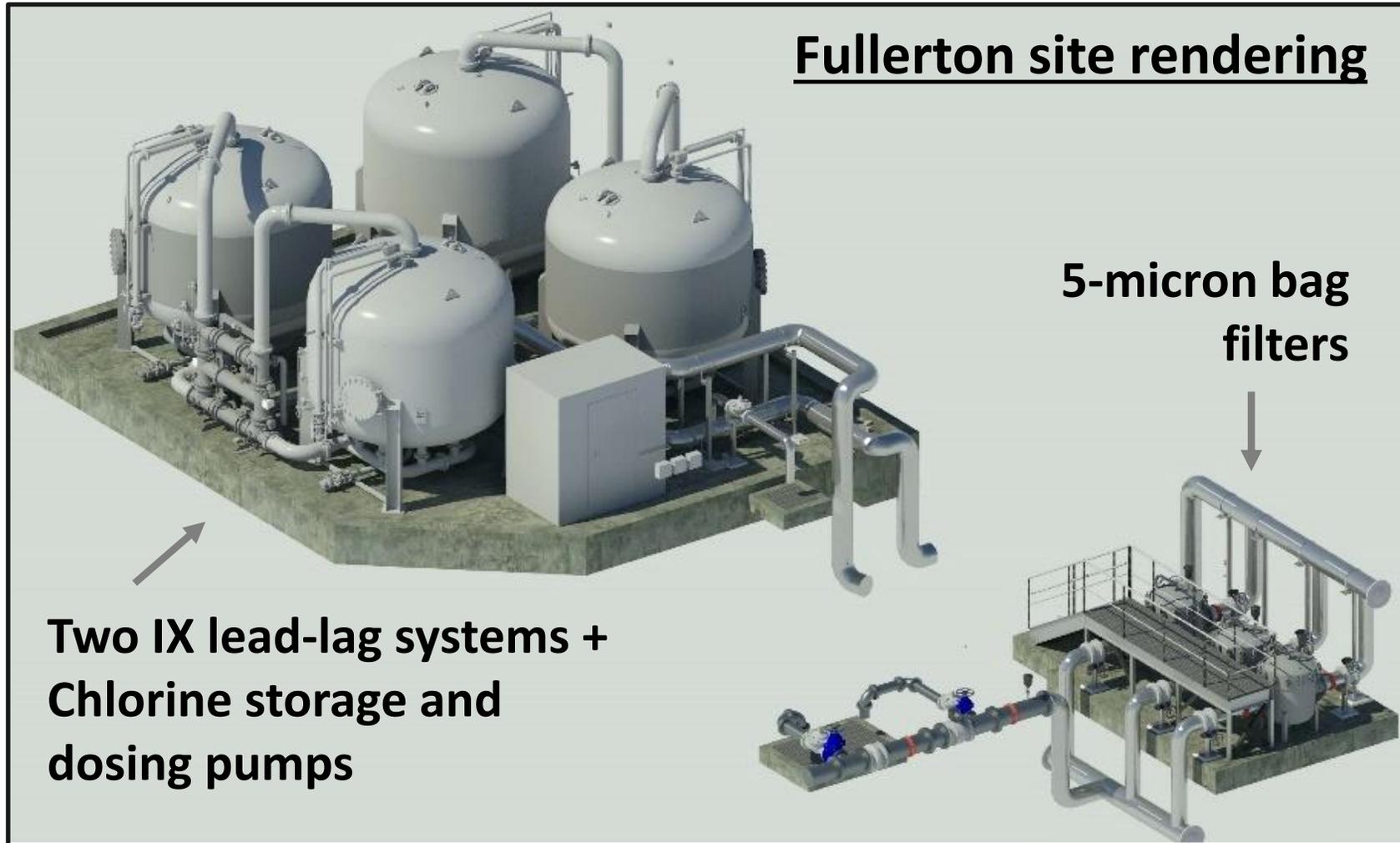
Different Phases of Pilot

PHASE II AND III ADSORBENTS



	No.	Company	Headquarters	Product Name	Type
PHASE II ONLINE	1	Evoqua 	Pittsburgh, PA	PSR2+	IX
	2			APR-2	IX
	3	LanXESS 	Cologne, Germany	Lewatit [®] TP108DW	IX
	4	ResinTech 	Camden, NJ	SIR-110-HP	IX
	5	Purolite 	King of Prussia, PA	Purofine D6515	IX
	6	CETCO 	Hoffman Estates, IL	FLUORO-SORB [®] FLEX	Alternative
PHASE III ONLINE	7	Calgon 	Moon Township, PA	CalRes 2304	IX
	8	Jacobi 	Kalmar, Sweden	PFCR-2	IX
	9	ECT2 	Portland, ME	Sorbix LC6	IX
	10	Confidential Resin	-	Leading manufacturer	IX
Future candidate	1	ABS Materials 	Wooster, OH	PQ-Osorb [®]	Alternative

How is Pilot Data Being Used? Supporting Initial IX Media Procurements & System Permits?



- IX selected for majority of the Orange County PFAS treatment systems thus far
- Based on bid pricing and pilot performance, Evoqua PSR2+ IX resin predominantly selected for the first 3 systems coming online
- **Thus, the pilot data was crucial in selecting treatment system media**

Serrano Water District well site

*Most Producers
have selected
IX due to
footprint
constraints*



Serrano Water District well site

*Treatment for 2 wells
(3,200 gpm max capacity)*



Yorba Linda Water District



Centralized treatment for 10 wells (25 mgd max capacity)
6 pre-filters
11 trains (= 22 vessels lead/lag)

Yorba Linda Water District



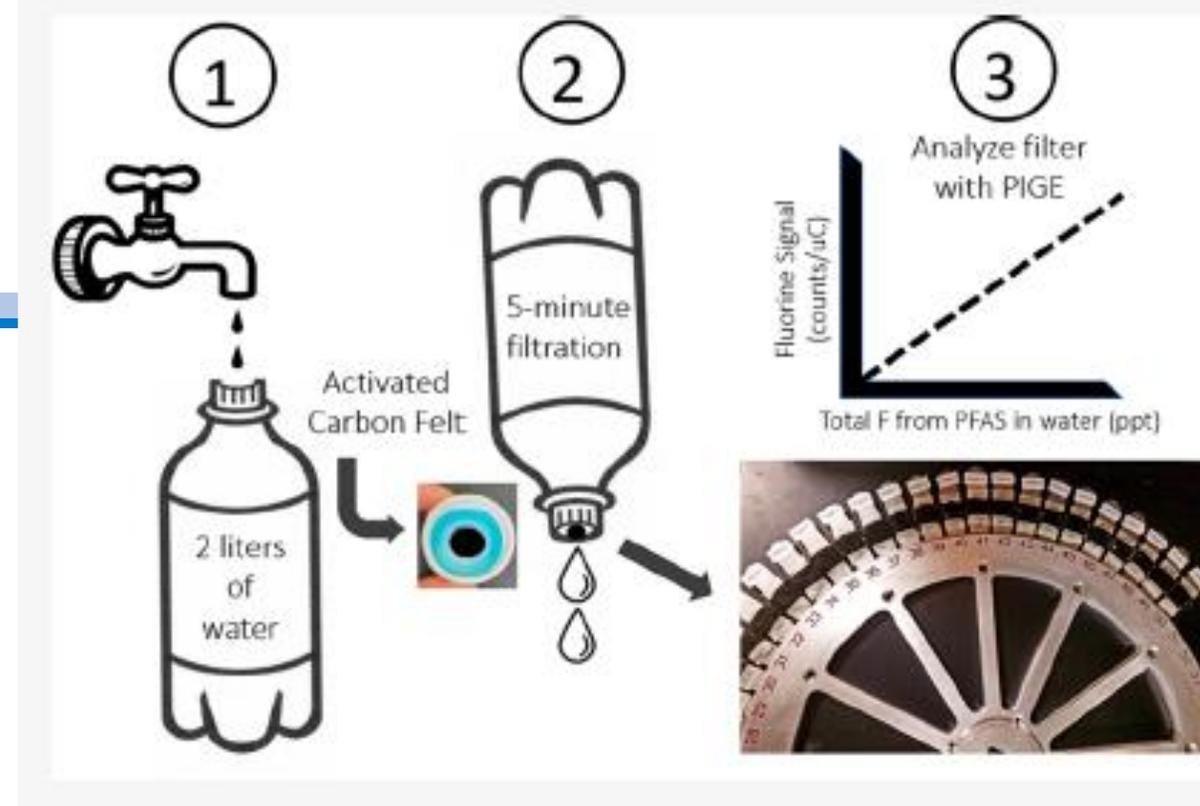
Centralized treatment for 10 wells (25 mgd max capacity)
6 pre-filters
11 trains (= 22 vessels lead/lag)

What Else?

Related Research Underway

<p>Funding Agency</p>			
<p>Project</p>	<p>Method development for screening for <u>Total PFAS</u> in water</p>	<p>Alternative methods to assess IX and AA at bench-scale</p>	<p><i>In-situ</i> removal of PFAS during MAR using horizontal PRB</p>
<p>Hopes and Dreams</p>	<p>Quickly, cheaply, measure sum PFAS</p>	<p>Rapid lab test, avoid lengthy piloting for IX and AA</p>	<p>Minimize PFAS introduced to aquifer via recharge projects</p>

Related Research Underway



Tighe et al., 2021 (ACS ES&T Water)

Method for Total PFAS by PIGE (Particle Induced Gamma Ray Emission)



- Project Lead:
- University of Notre Dame

WRF Project title: *Application of a Novel Method to Estimate Total PFAS Content in Water – #5102*

Thank you!!

More Information: Meeta Pannu, mpannu@ocwd.com



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