Occurrence and Removal of PFAS from Water

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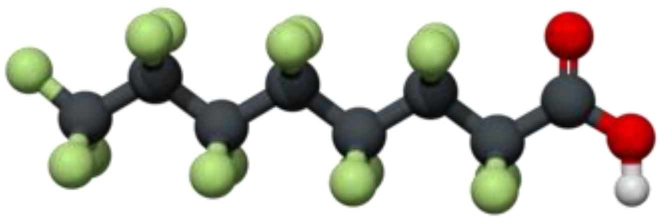
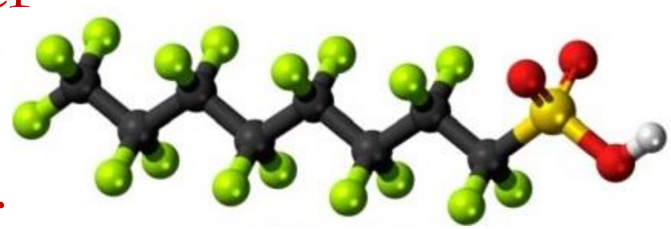
OTCO Water Laboratory Workshop

May 15, 2019

Agenda

- What is PFAS?
- Occurrence of PFAS in US/Globally
- Common PFAS chemicals
- Chemistry of PFOA and PFOS
- Health risks associated with PFAS
- Regulatory impacts from PFAS in water
- General removal technologies
- Effective removal of PFAS from water
  - Proven technologies and results





PFAS

- **P F A S** - Perfluoroalkyl and polyfluoroalkyl substances
- Industrial and commercial chemicals used in manufacturing consumer products
  - 3M Company, DuPont, Chemours, Solvay, Archroma, Asahi Glass, Arkema, Daikin, and Dyneon all made PFAS for industrial, commercial, military, and agricultural products
- Ingredients in Teflon, Scotch Gard, water-repellents, grease repellents, stain-resistant carpeting and upholstery, non-stick cookware, food wrappers and containers, microwave popcorn bags, high performance plastics, electronics, firefighting foams, sealants, etc.
- Possibly 3,500 different PFAS chemicals in the environment

PFAS

- Fluorinated carbons with an attached functional group
  - C-F strongest bond in chemistry (544 kJ/mol)
  - Extremely resistant to degradation
    - Half-lives are several years
  - Bioaccumulates in human blood and microorganism cells
    - Levels increase with each subsequent exposure
    - Accumulates in sludge and biological processes
    - Toxicity can be reached after multiple exposures
    - 2003, average Americans had 4 ppb to 5 ppb blood serum levels, today 99% likely have PFAS in blood




PFAS

- Highly water soluble
- Not removed by conventional treatment processes
  - Includes water and wastewater treatment
  - Passes through processes into final product
    - Wastewater discharges are considered a primary contributor of PFAS to source waters
    - Land supplication of biosolids considered a primary source of PFAS in soil
      - PFAS passed on to plants grown in soil

PFAS

- Industrial contamination
  - Likely responsible for most PFAS globally
- Landfill contamination
  - Not equipped to treat PFAS
    - Leachate discharges to the environment
- Wastewater plants
  - Not equipped to treat PFAS
    - Effluent discharges to the environment
    - Sludge disposal recycles PFAS to the environment
- Agricultural and stormwater runoff
  - Contains PFAS levels that are not monitored

PFAS

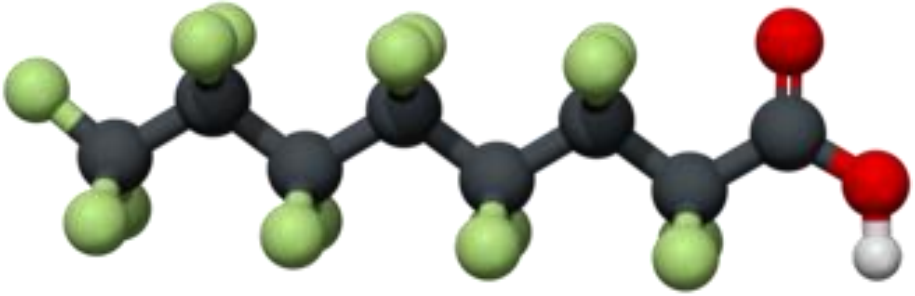
- Many substances no longer manufactured
  - Replaced with other products like Gen X (fluoropolymers)
    - USEPA now states that Gen X chemicals are as toxic as the predecessor chemicals
- Possibly one of the next big issues in drinking water
  - Numerous contamination sites across US
  - More than 3,500 law suits filed against previous manufacturers
    - DuPont has paid more than $1 billion in penalties/clean-up activities
  - USEPA established health advisory levels in 2009 and again in 2016

PFAS

- PFOA and PFOS most common PFAS chemicals
  - Primary focus of EPA actions related to PFAS in drinking water
    - Perfluorooctanoic acid (PFOA)
    - Perfluorooctane sulfonic acid (PFOS)
      - Current health advisory levels – combined 70 ppt
- Other PFAS Chemicals
  - There are numerous PFAS chemicals that have related health effects
  - Future regulatory requirements could include multiple PFAS chemicals, Gen X chemicals, or degradation byproducts

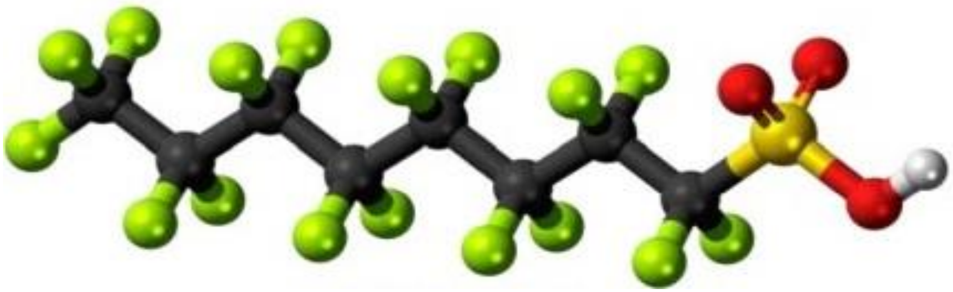
PFOA

- $C_8HF_{15}O_2$
  - Linear polymeric molecule
  - Commonly called C8
- Molecular weight
  - 414.1 grams/mole
- Water solubility
  - 9,500 mg/L
- Estimated half-lives
  - 3.4 years in human blood
  - 41 years in water



Carbons with attached fluorine atoms and a carboxyl functional group forming an acid

PFOS



Carbons with attached fluorine atoms and a sulfonated functional group forming an acid

- $C_8HF_{17}O_3S$
  - Linear polymeric molecule
- Molecular weight
  - 500.1 grams/mole
- Water solubility
  - 570 mg/L
- Estimated half-lives
  - 5.4 years in human blood
  - 92 years in water

Other water soluble PFAS

- Perfluorobutanoic acid (PFBA)
  - $C_4HF_{15}O_2$
  - Water solubility 214,000 mg/L
- Perfluorohexanoic acid (PFHxA)
  - $C_6HF_{11}O_2$
  - Water solubility 15,700 mg/L
- Perfluoroheptanoic acid (PFHpA)
  - $C_7HF_{13}O_2$
  - Water solubility 437,000 mg/L
- Perfluorodecanoic acid (PFDeA)
  - $C_{10}HF_{19}O_2$
  - Water solubility 260 mg/L

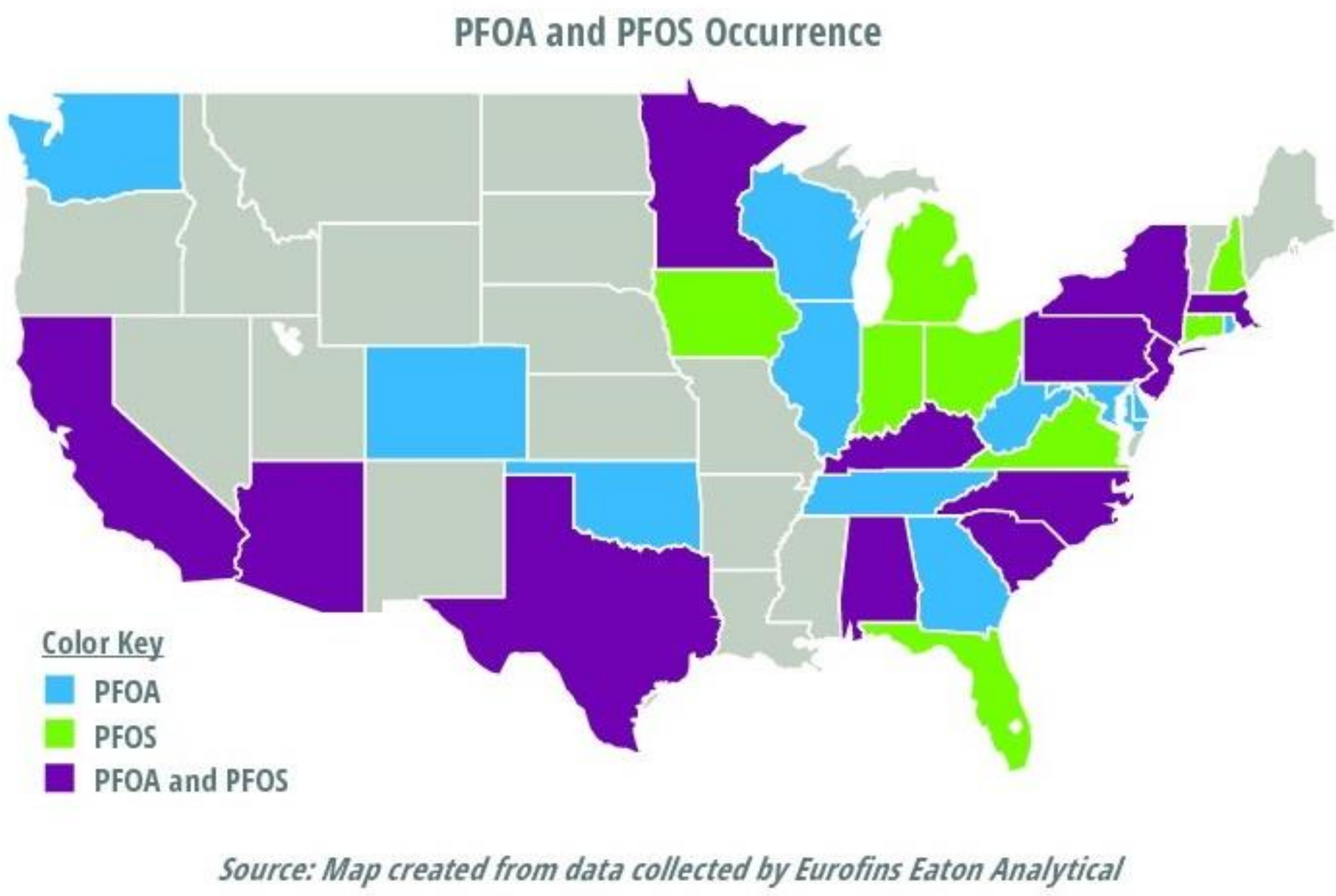
Paper packaging, film manufacture, stain-resistant fabrics

Stain-proof and grease-proof coating breakdown byproducts

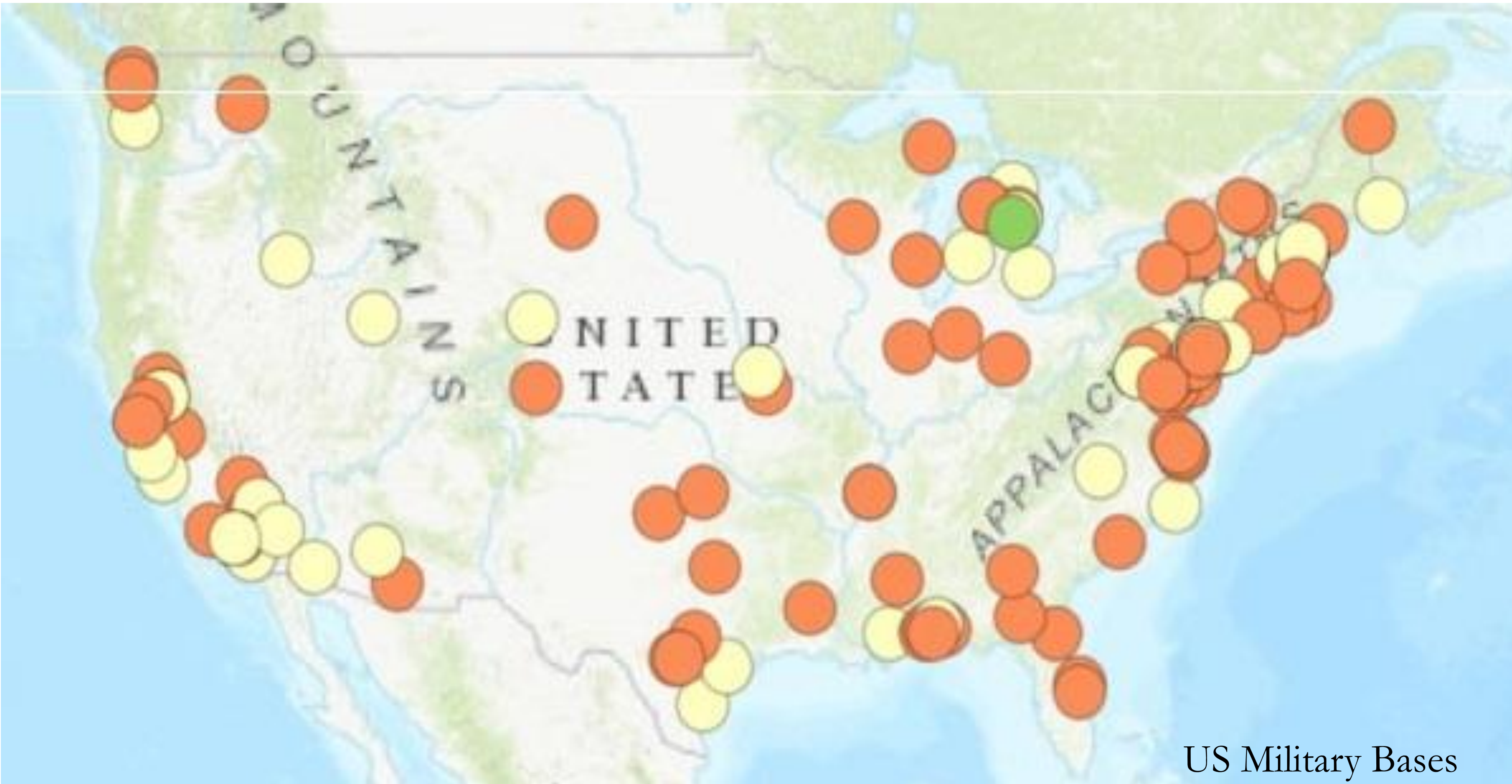
Occurrence in US

- PFAS is fairly wide-spread across the eastern US
  - Particularly Michigan and New Jersey
- Some PFAS along Western/Southern border states
- 30 states either established or adopted regulatory limits for PFAS in water
  - Others waiting for EPA to regulate
- Numerous military bases across the US have ground water contamination from firefighting foams
  - Practice facilities for firefighting military vehicles

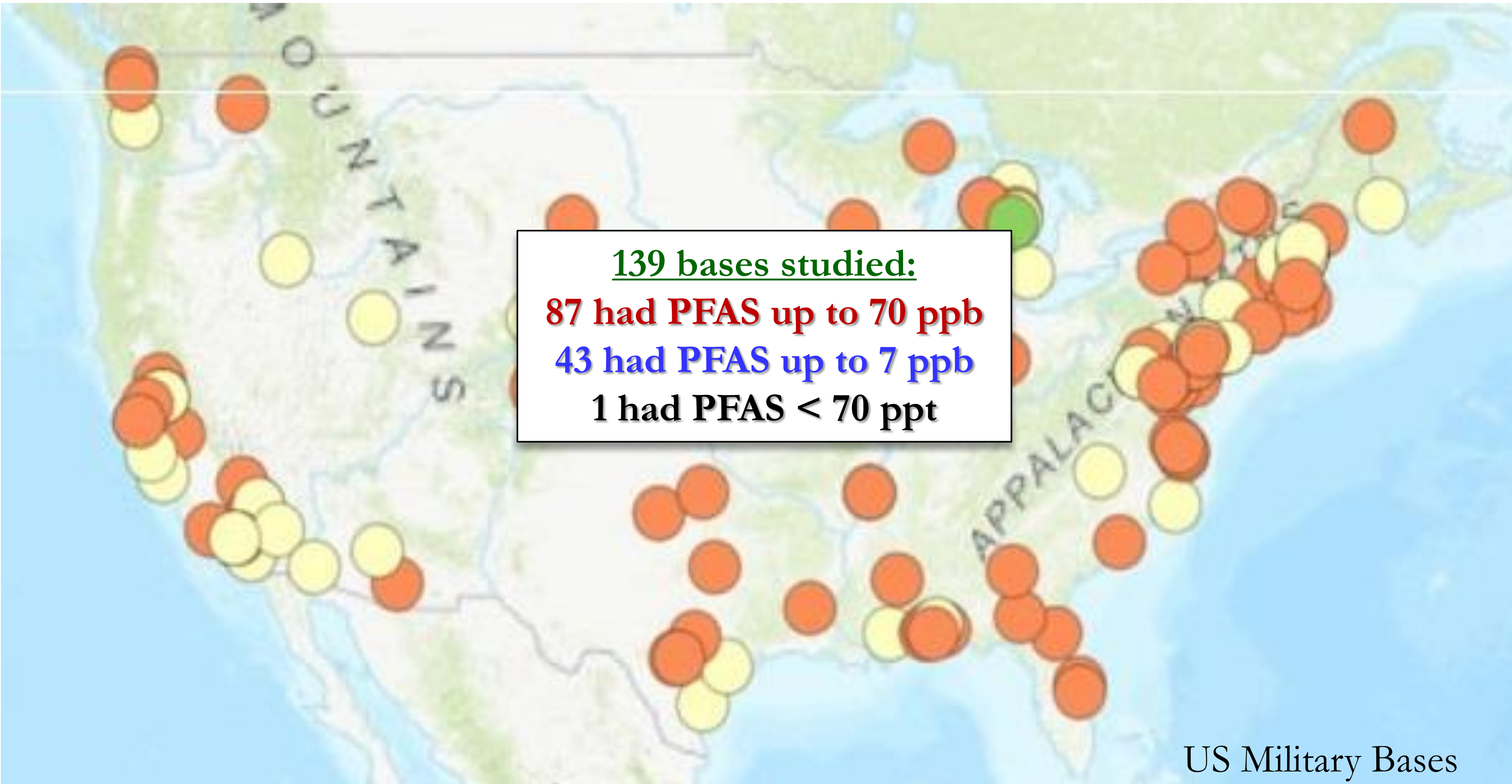
Occurrence in US



Occurrence in US



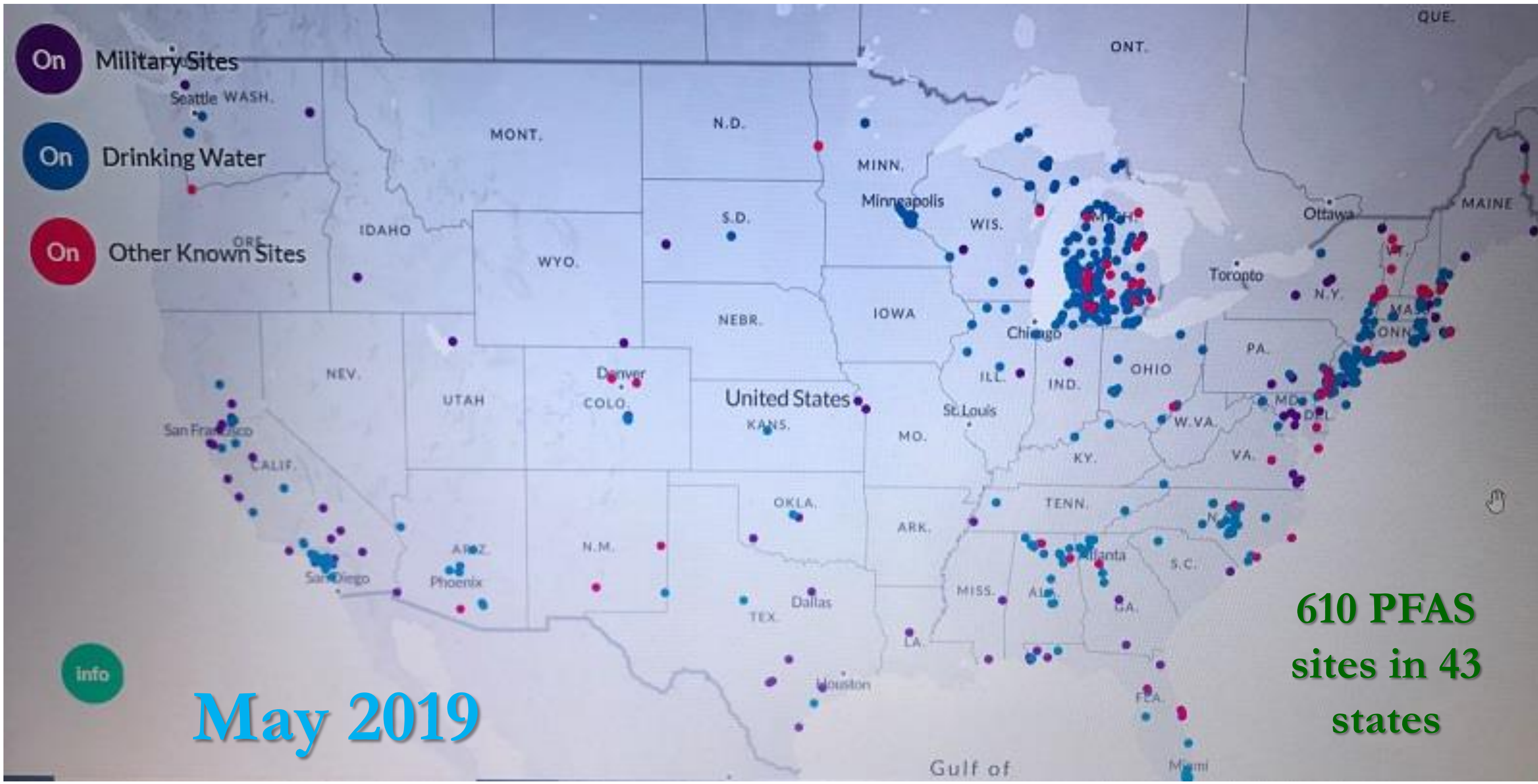
Occurrence in US



Occurrence in US

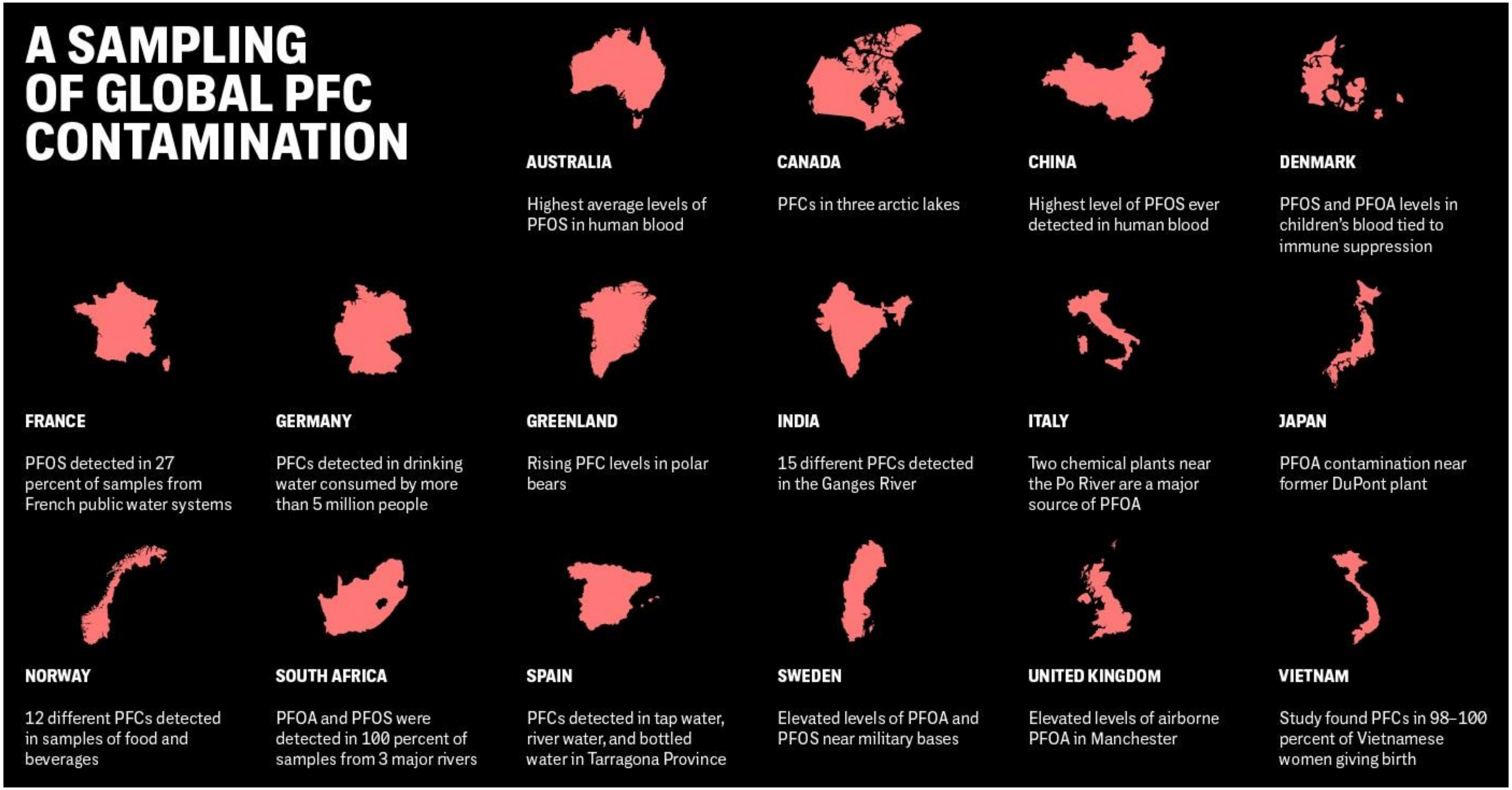
EPA first alerted to PFAS in Ohio River from Parkersburg, WV (EWG)

Occurrence in US



2019 EWG / Northern University

Occurrence Globally



Regulatory Impacts

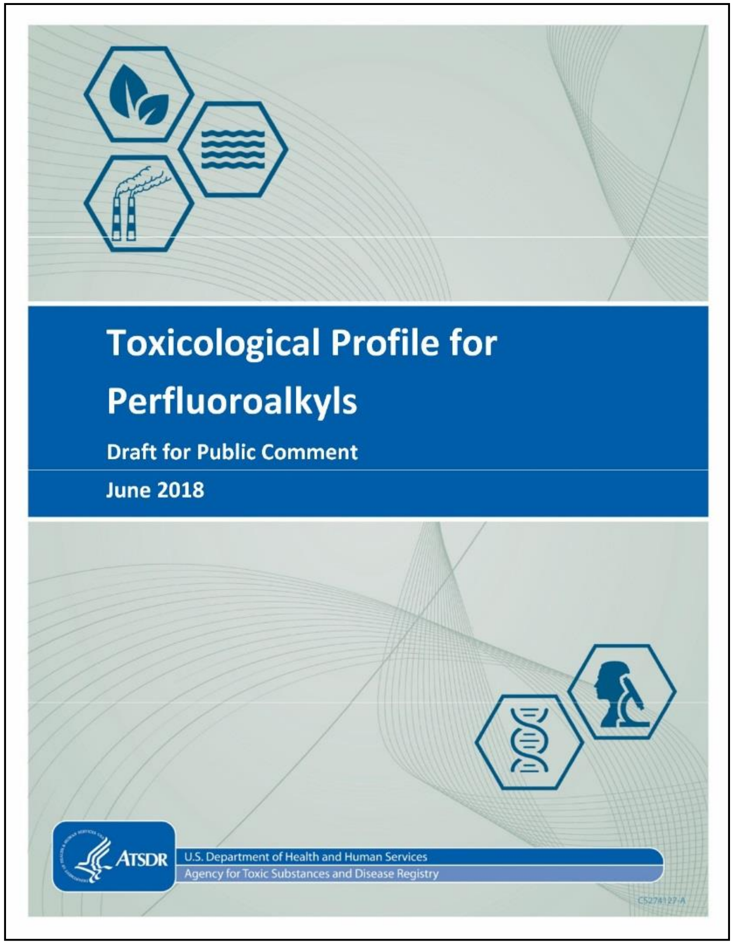
- USEPA first alerted to PFAS 2001
  - Large contamination site in Parkersburg, WV storing 7,100 tons of PFAS-laden sludge
  - Site adjacent to DuPont manufacturing plant
  - Led to ground water contamination of area wells
    - PFOA traveled under Ohio River to Little Hocking, Ohio
- 2009 EPA established provisional health advisory levels
  - PFOA 0.4 µg/L (400 ng/L)
  - PFOS 0.2 µg/L (200 ng/L)
    - Based on science known at the time

Regulatory Impacts

- 2012 EPA placed six perfluorinated compounds on UCMR 3 monitoring schedule
  - Included PFOA and PFOS as well as PFNA, PFHxS, PFHpA, and PFBS
  - Monitoring conducted for water systems in 2013-2015
    - 2% US had PFAS >20 ng/L, 0.3% US had PFAS >70 ng/L
- 2016 EPA announced new health advisory levels
  - PFOA and PFOS life time advisory 70 ng/L combined
    - PFOA and PFOS found in human blood of nearly every person tested
    - Consumer products and food likely major contributors of exposure
  - Considerations for regulating PFOA and PFOS

Regulatory Impacts

- US Department of Health and Human Services (DHHS)
  - 2018 Toxicological Profile for Perfluoroalkyls
    - Obtaining public comments
    - Published minimum risk levels for 4 compounds
    - PFOA 3 ng/L (ppt)
    - PFOS 2 ng/L
    - PFHxS 20 ng/L
    - PFNA 3 ng/L



Regulatory Impacts

State	Regulatory Limits
California	PFOA 14 ppt, PFOS 13 ppt
Minnesota	PFOA 35 ppt, PFOS 27 ppt
New Jersey	PFOA 13 ppt, PFOS 14 ppt, PFNA 13 ppt
Vermont	20 ppt any combination of 5 compounds PFOA, PFOS, PFHpA, PFHxS, PFNA
North Carolina	Provisional goal 140 ppt
Wisconsin, Montana, Mississippi, Pennsylvania, Washington	Developing PFAS limits soon

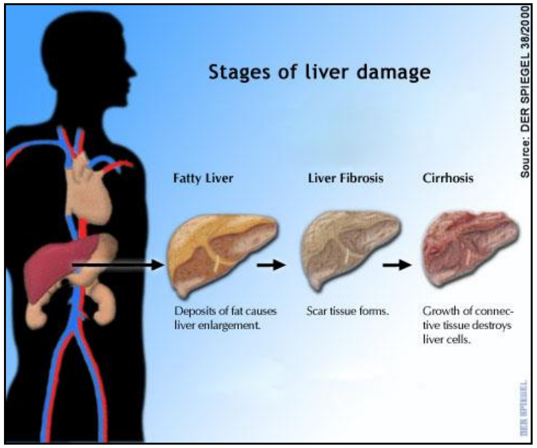
Regulatory Impacts

Follow USEPA Health Advisory Limits 70 ppt		
Alabama	Kentucky	New Mexico
Alaska	Idaho	Nevada
Arizona	Indiana	Oregon
Colorado	Massachusetts	Virginia
Connecticut	Maine	West Virginia
Florida	Michigan	
Hawaii	New Hampshire	

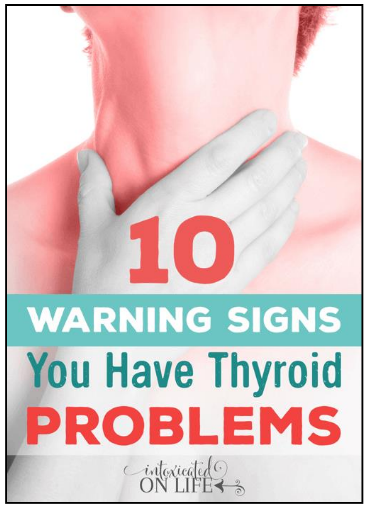
Remaining states waiting for USEPA regulatory actions

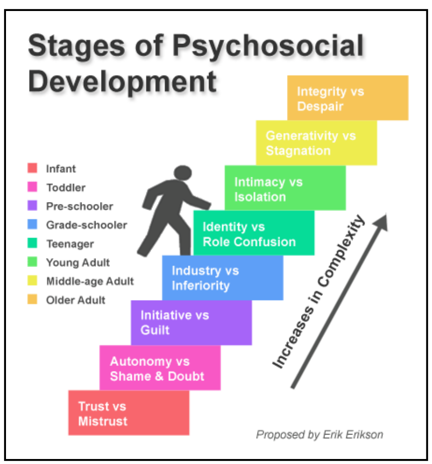
Health Effects USDHHS 2018

- Liver damage
  - PFOA, PFOS, PFHxS, PFHpA, PFNA, PFDA, PFUA, PFBA, PFBuS
- High cholesterol
  - PFOA, PFOS, PFNA, PFDA
- Pregnancy-induced hypertension (cardiovascular effects)
  - PFOA, PFOS



Health Effects USDHHS 2018





- Thyroid (endocrine) disease
  - PFOA, PFOS
- Immune effects
  - PFOA, PFOS, PFHxS, PFDA
- Reproductive effects (decreased fertility)
  - PFOA, PFOS
- Developmental effects
  - PFOA, PFOS PFHxS, PFNA, PFDA, PFUA, PFBA

General Removal Technologies

- Good treatment summary WRF Project 4322 (2016)
  - Evaluation of 15 full-scale operations across US
    - Some were conventional treatment
    - Some had advanced treatment processes
    - Evaluated reductions in 23 PFAS chemicals by process train
  - Bench-scale evaluations for GAC and NF/RO
  - Provided general summary for a number of processes and ability to remove PFAS chemicals
  - Summary stated conventional treatment, oxidation processes (including AOP), not effective for PFAS removals
    - Sulfonated compounds easier to remove than carboxylated compounds
    - Compounds with ≥8 carbons easier to remove than those with <8
    - PFAS wastes need to be properly treated or disposed

General Removal Technologies

TABLE 4
GENERAL REMOVAL EFFICIENCIES FROM 2016 WRF PUBLICATION

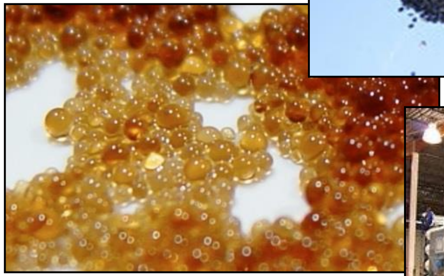
Compound	MW	Aeration	Coag/ DAF	Coag/Floc-Sed/Filt	AEX	GAC	NF	RO	Oxid.
PFOA	414	<10%	<10%	<10%	10% -90%	>90%	>90%	>90%	<10%
PFOS	500	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
PFBA	214	<10%	<10%	<10%	<10%	<10%	>90%	>90%	<10%
PFPeA	264	<10%	<10%	<10%	<10%	10% -90%	>90%	>90%	<10%
PFHxA	314	<10%	<10%	<10%	<10%	10% -90%	>90%	>90%	<10%
PFHpA	364	<10%	<10%	<10%	10% -90%	>90%	>90%	>90%	<10%
PFNA	464	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
PFDA	514	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
PFBS	300	<10%	<10%	<10%	10% -90%	>90%	>90%	>90%	<10%
PFHxS	400	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
FOSA	499	10% -90%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
N-MeFOSAA	571	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
N-EtFOSAA	585	<10%	<10%	<10%	>90%	>90%	>90%	>90%	<10%
Legend	<10%	10% -90%	>90%						

Coag.-coagulation DAF-dissolved air flotation Filt – granular or membrane filtration AEX – anion exchange NF – nanofiltration membranes OR – reverse osmosis membranes Oxid. – oxidation processes including AOP

Generally 300 Daltons MWCO for Membranes

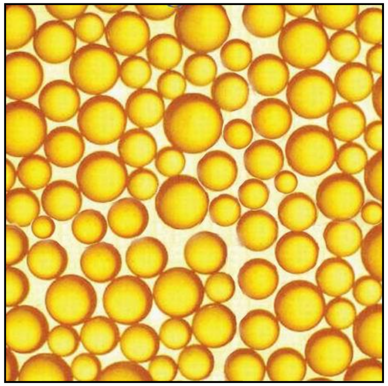
Specific Removal Technologies

- Treatment information gathered and presented
  - Anion exchange adsorption
  - GAC adsorption treatment
  - NF/RO membranes



Anion Exchange Adsorption

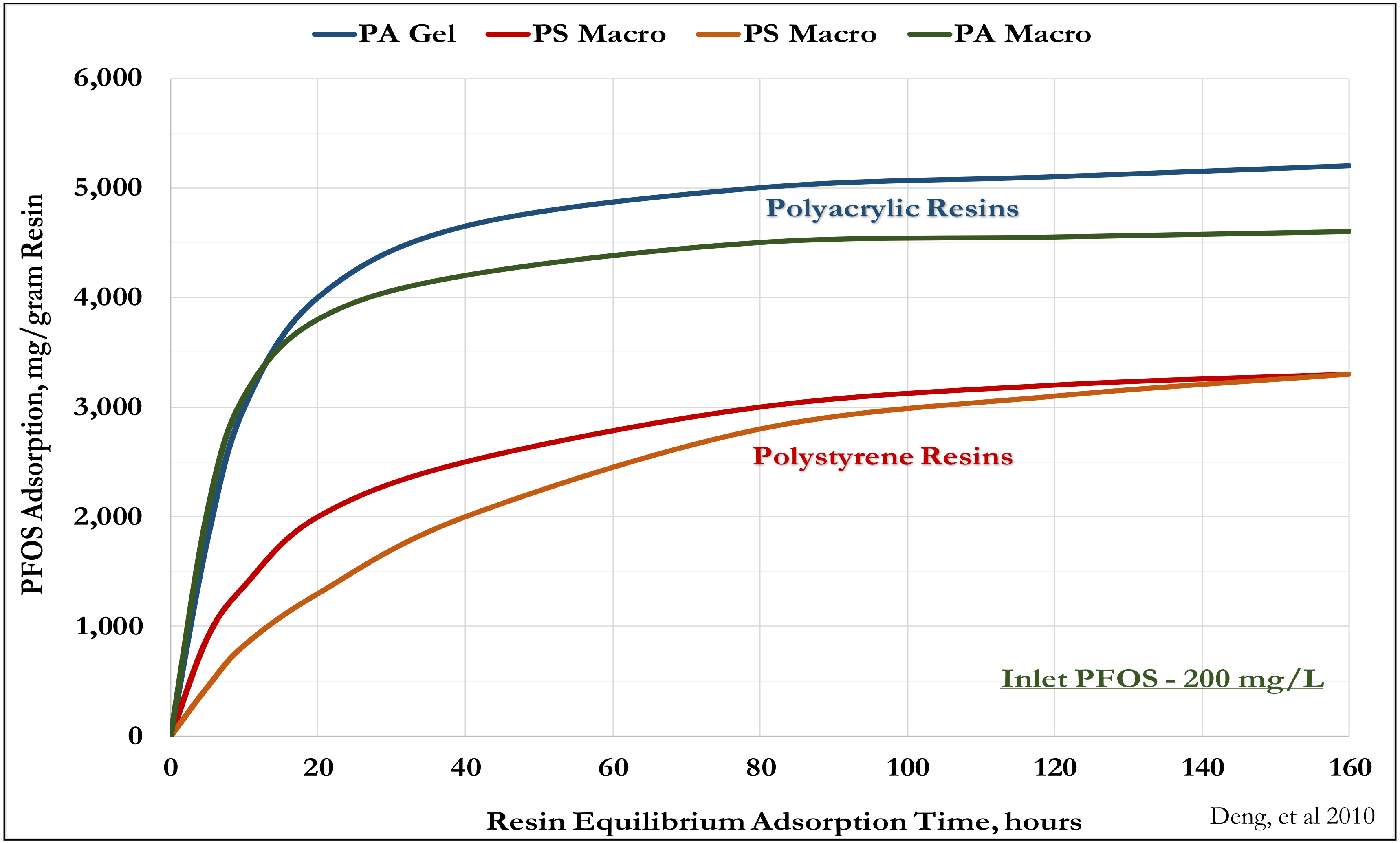
- Ion exchange process where anions are exchanged on a media surface through adsorption
  - Regeneration with NaCl or HCl common
- Macroporous resins and microporous gel resins available
  - EBCT usually 1.5 minutes to 4 minutes
- PFAS adsorption occurs until exchangeable ions depleted
  - Literature states this can be several thousand bed volumes
  - Removes all types of PFAS



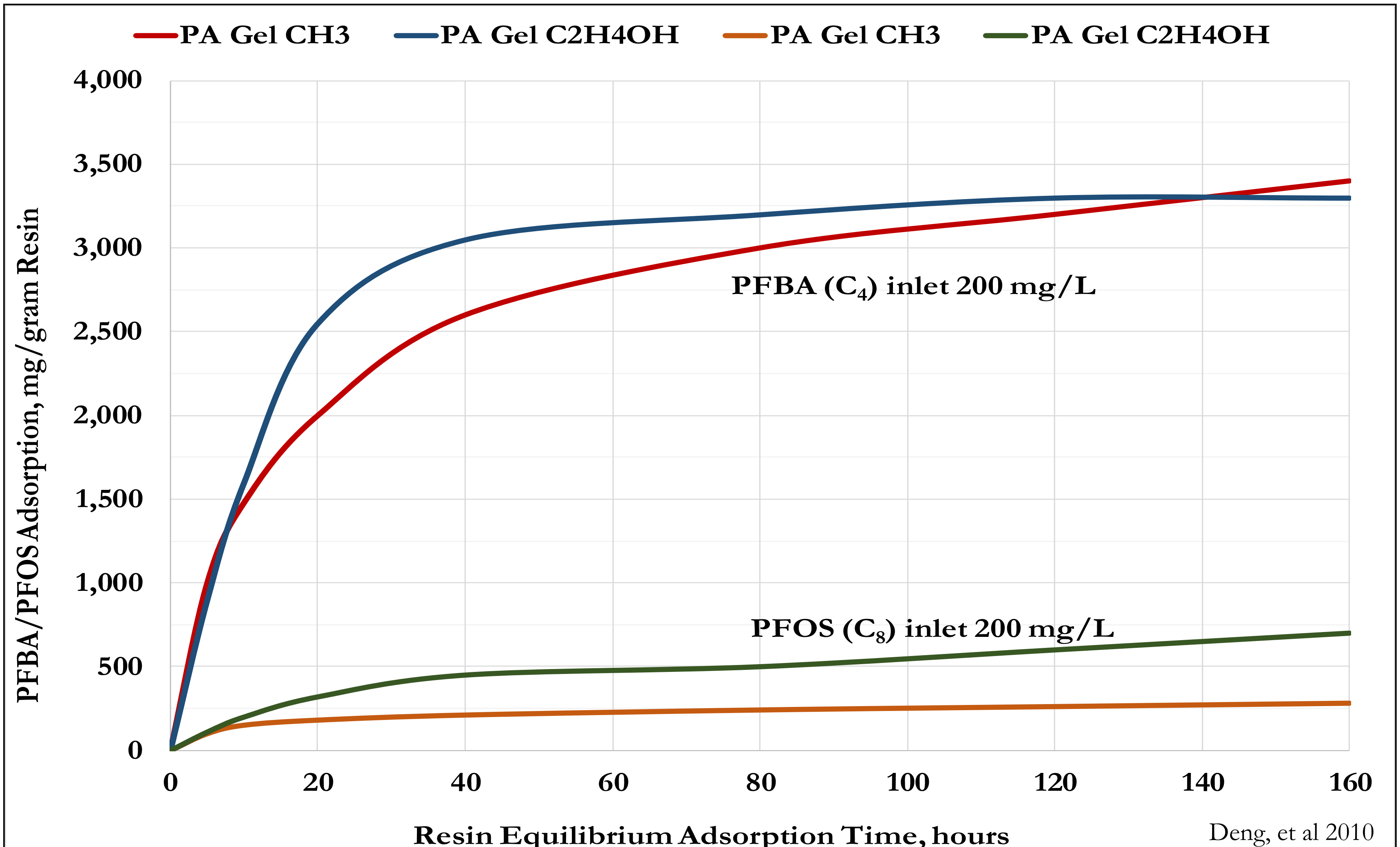
Anion Exchange Adsorption

- Deng, et al (2010) resin comparisons
  - Smaller diameter resins increase adsorption rate
  - Polyacrylic resins perform better than polystyrene resins
  - Macroporous resins react much faster and have more removal capacity than gel-type resins
  - Long-chain materials more easily removed than short-chain compounds
  - pH influences adsorption onto polyacrylic resins, but not polystyrene resins
  - Competition with other anions exists reducing overall removal capacity (SO_4, NO_3, HCO_3, TOC)
  - Regeneration with methanol/salt solution may needed periodically to elute PFAS from resin materials

Anion Exchange Adsorption



Anion Exchange Adsorption



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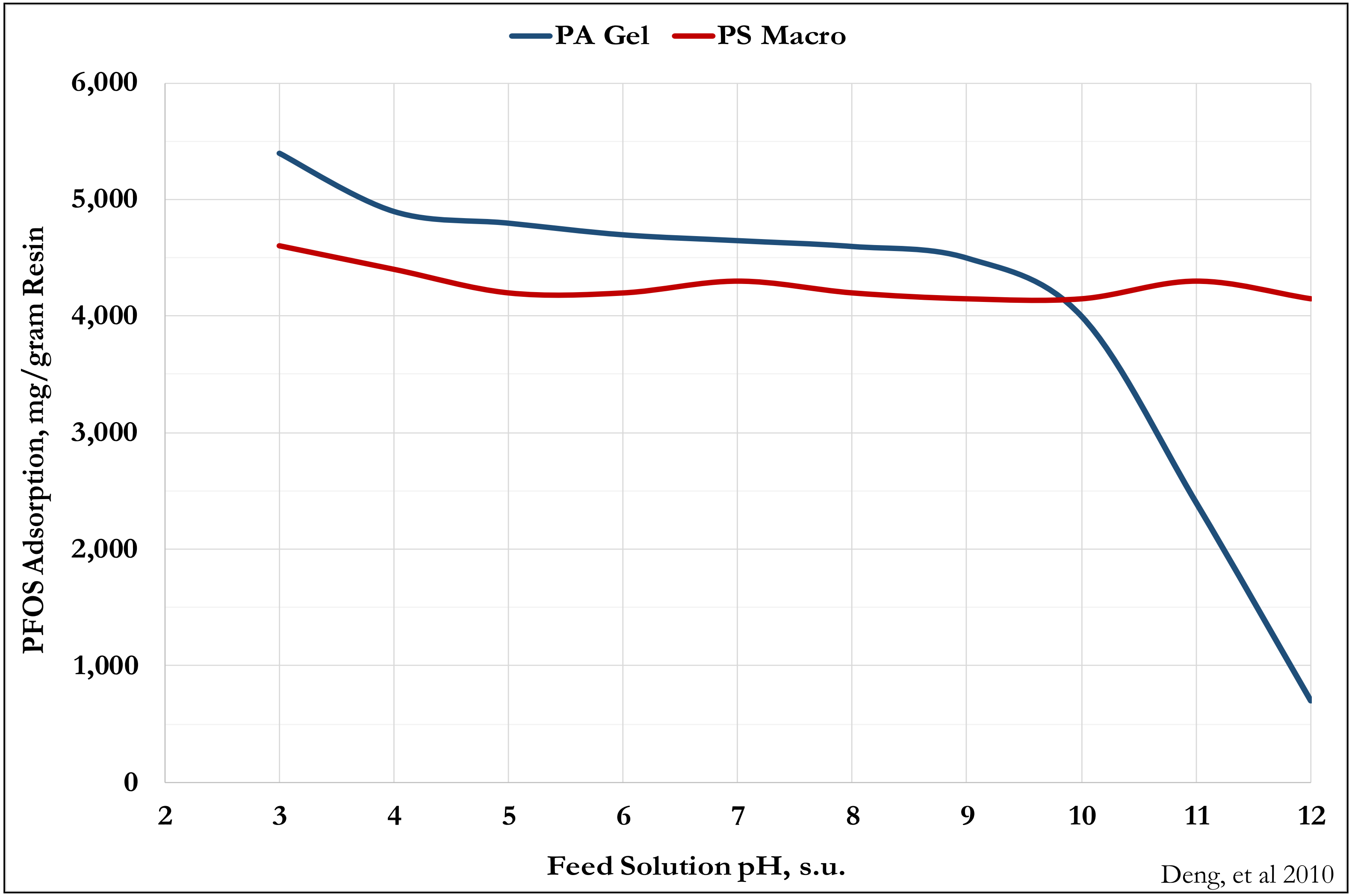

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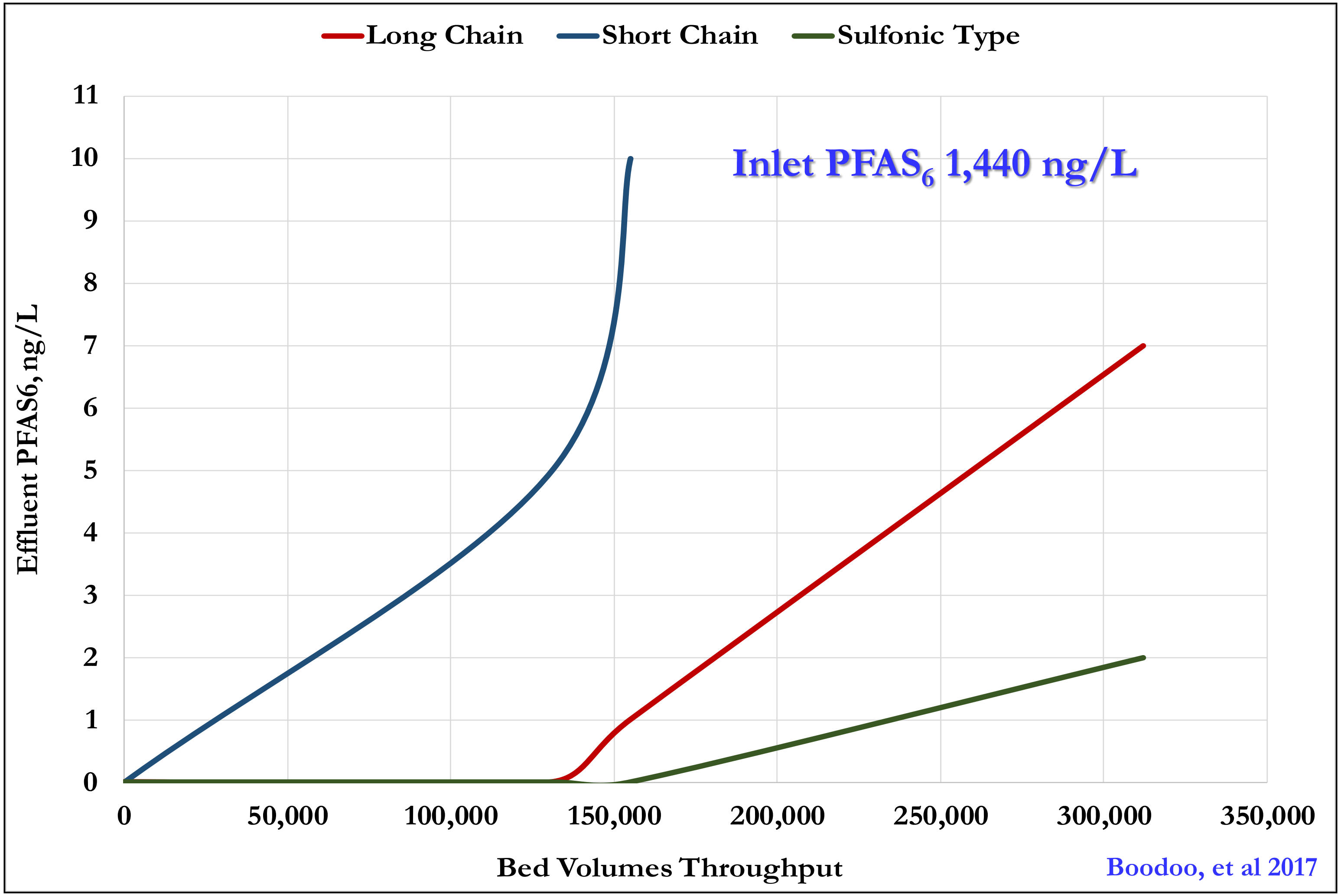

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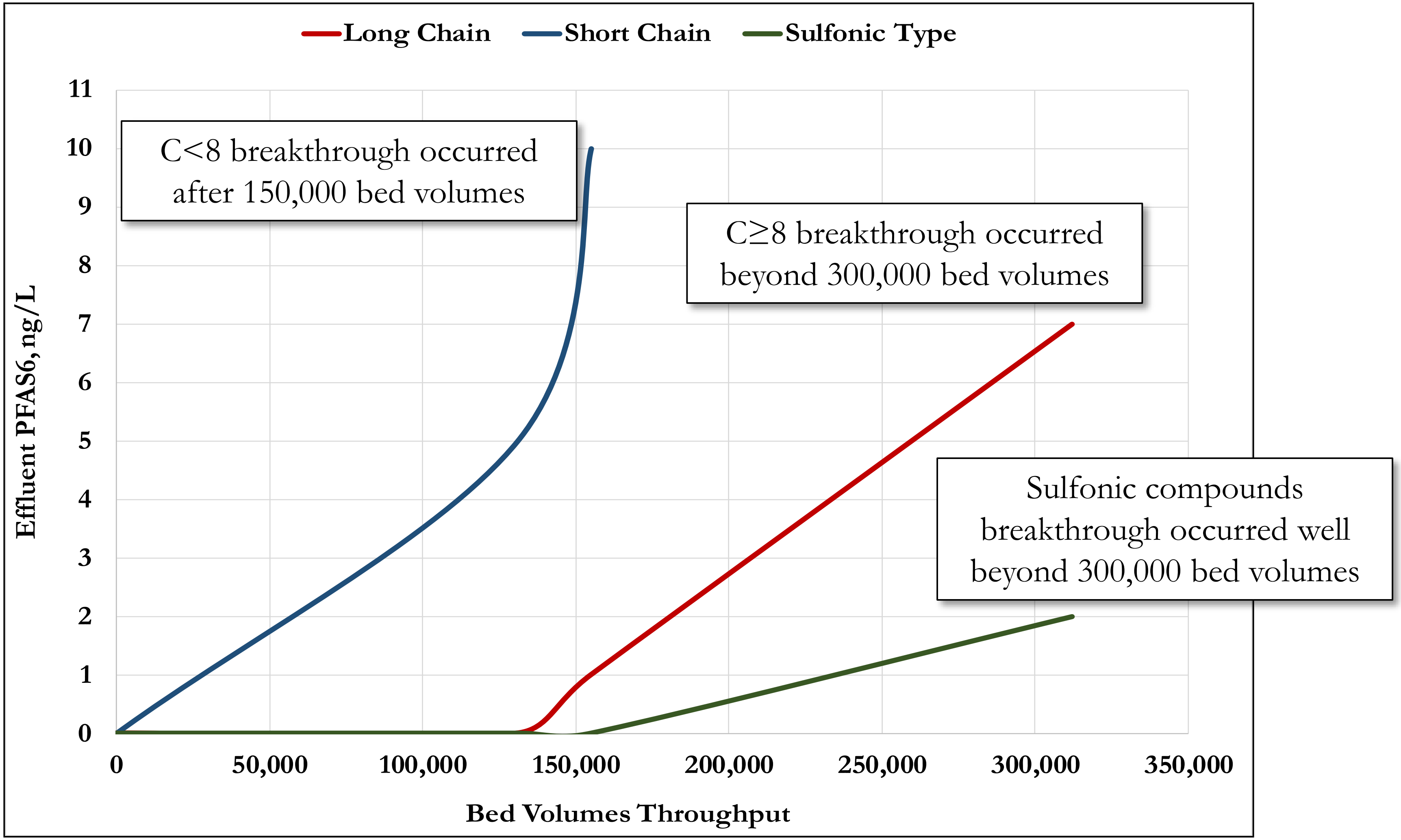


Anion Exchange Adsorption

- Bed volume to run cycle time (assuming 500 gpm)
  - 100,000 BV ≈ 26 days
  - 300,000 BV ≈ 80 days
  - 500,000 BV ≈ 130 days
- Regeneration elutes PFAS from resin
  - Produces high concentration of PFAS in spent brine waste
  - Waste must be either treated to remove PFAS or properly disposal
  - Waste considered hazardous, incineration may be best disposal method
    - Likely restricted to about 5 mgd capacity plants to reduce large waste volumes and handling/disposal issues

NF/RO membranes

- Tight NF or RO membranes needed for low MW
  - MWCO suggested at 300 Daltons
- Membrane rejection 90% to 99% typical
  - Reduction in all types of PFAS chemicals
  - Typical recovery 80% to 85%
  - Typical concentrate 15% to 20%
- NOM must be accounted for in operations
  - Impacts recovery and concentrate operations
  - Impacts membrane cleaning cycles
- Concentrate streams
  - High concentrations of PFAS, considered hazardous waste
  - Must be treated before discharge or incineration

NF/RO membranes

REVERSE OSMOSIS MEMBRANE OPERATING DATA South East Queensland, Australia 2011, Thompson, et al Results given in ng/L concentrations.					
RO Process	**PFOA**	**PFOS**	**PFHxS**	**PFHxA**	**PFDA**
Feed Water	22	30	35	14	1.9
Concentrate	162	157	217	100	18
Permeate	ND	ND	ND	ND	ND

- 5 PFAS compounds identified in feed water
- Concentrate stream increased PFAS by 700%
- Permeate normally non-detectable PFAS levels
- Feed water TOC averaged <1 mg/L

NF/RO membranes

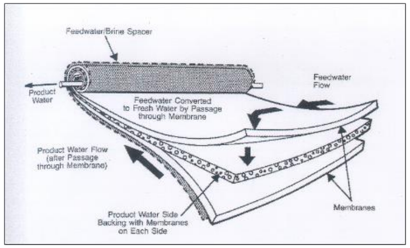
REVERSE OSMOSIS MEMBRANE OPERATING DATA Spanish Drinking Water, 2013, Flores, et al 50% RO Treatment/50% GAC Treatment Results given in ng/L concentrations.					
RO Process	PFOA	PFOS	GAC Process	PFOA	PFOS
Feed Water	15	104	Feed Water	15	104
Concentrate	98	659			
Permeate	ND	ND	Effluent	4.7	22
Blended Finished Water				**2.4**	**11**

- Conventional treatment and GAC blended with conventional treatment and RO (50/50 treatment trains)
- Concentrate stream increased PFAS by more than 630%
- Permeate normally non-detectable PFAS levels

NF/RO membranes

REVERSE OSMOSIS OF WASTEWATER FOR POTABLE REUSE FOLLOWING CONVENTIONAL ACTIVATED SLUDGE Glover, et al 2018 Las Vegas, Nevada Feed Water Ranged from 8 ng/L to 82 ng/L		
PFAS Chemical	Carbons	% Removal Permeate
PFBA	4	79%
PFBS	4	ND
PFPnA	5	95%
PFHxS	6	80%
PFHxA	6	96%
PFHpA	7	87%
PFOA	8	77%
PFOS	8	71%
PFNA	9	77%
PFDA	10	67%
PFDS	10	ND
N-MeFOSAA	11	ND

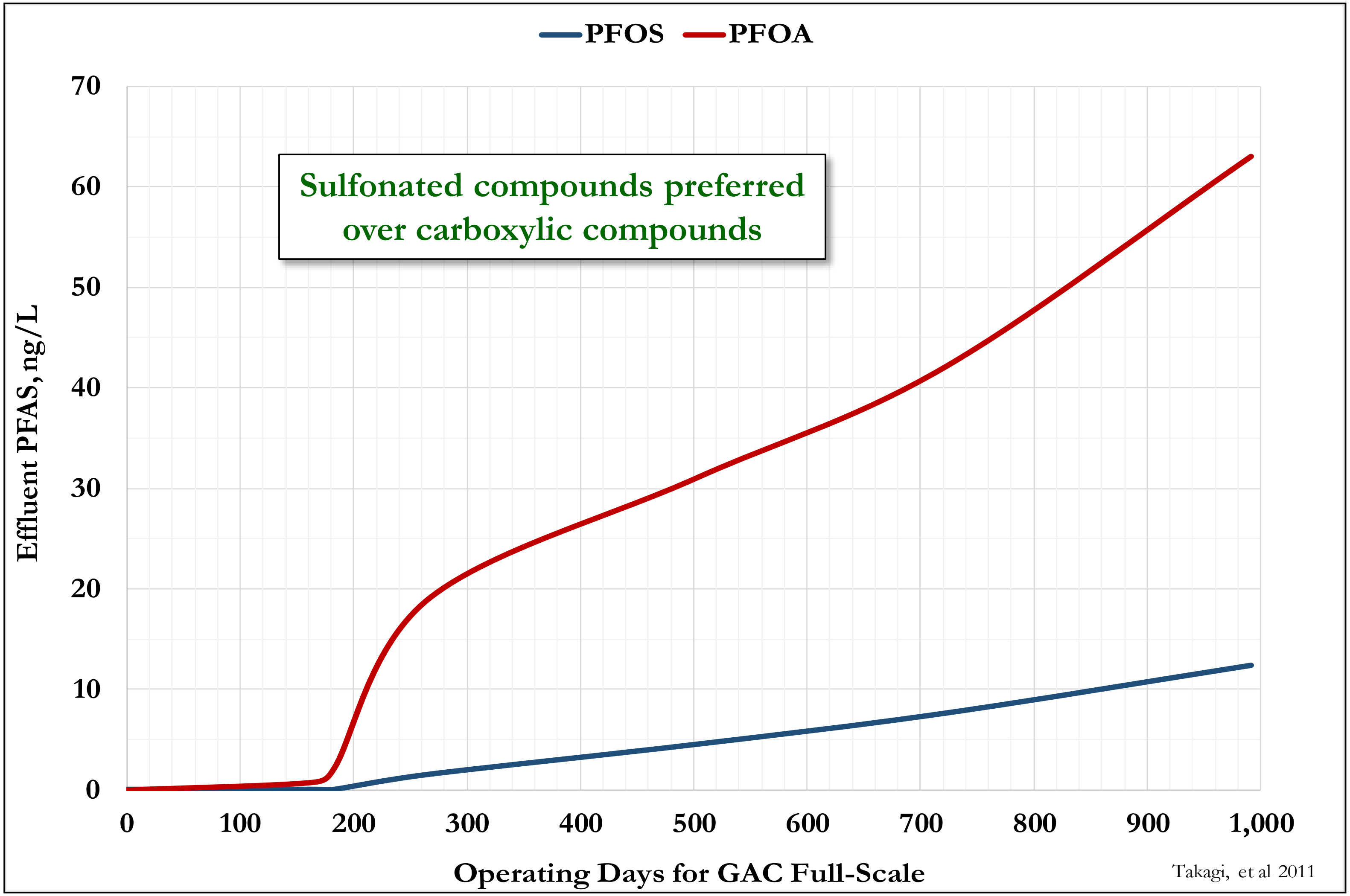
- Feed water concentration typically 227 ng/L combined
- Percent reductions associated with **MRL (method reporting limit)** to represent worst-case operations
- Permeate normally non-detectable PFAS levels



GAC Adsorption

- Proper selection of GAC is important to successful treatment
  - Need good distribution of pore sizes to maximize adsorption
  - NOM competes for adsorption sites
    - TOC usually breaks through before PFAS
- EBCT should be 10 minutes or greater
  - Single pass system or lead/lag operations available
    - <0.5 μg/L PFAS, single pass system may be sufficient
    - ≥0.5 μg/L PFAS, lead/lag systems may be necessary
- Limitations may exist for compounds < 400 g/mole MW
  - Breakthrough quicker and reach equilibrium faster
  - Desorption occurs as higher carbons compete for sites

GAC Adsorption



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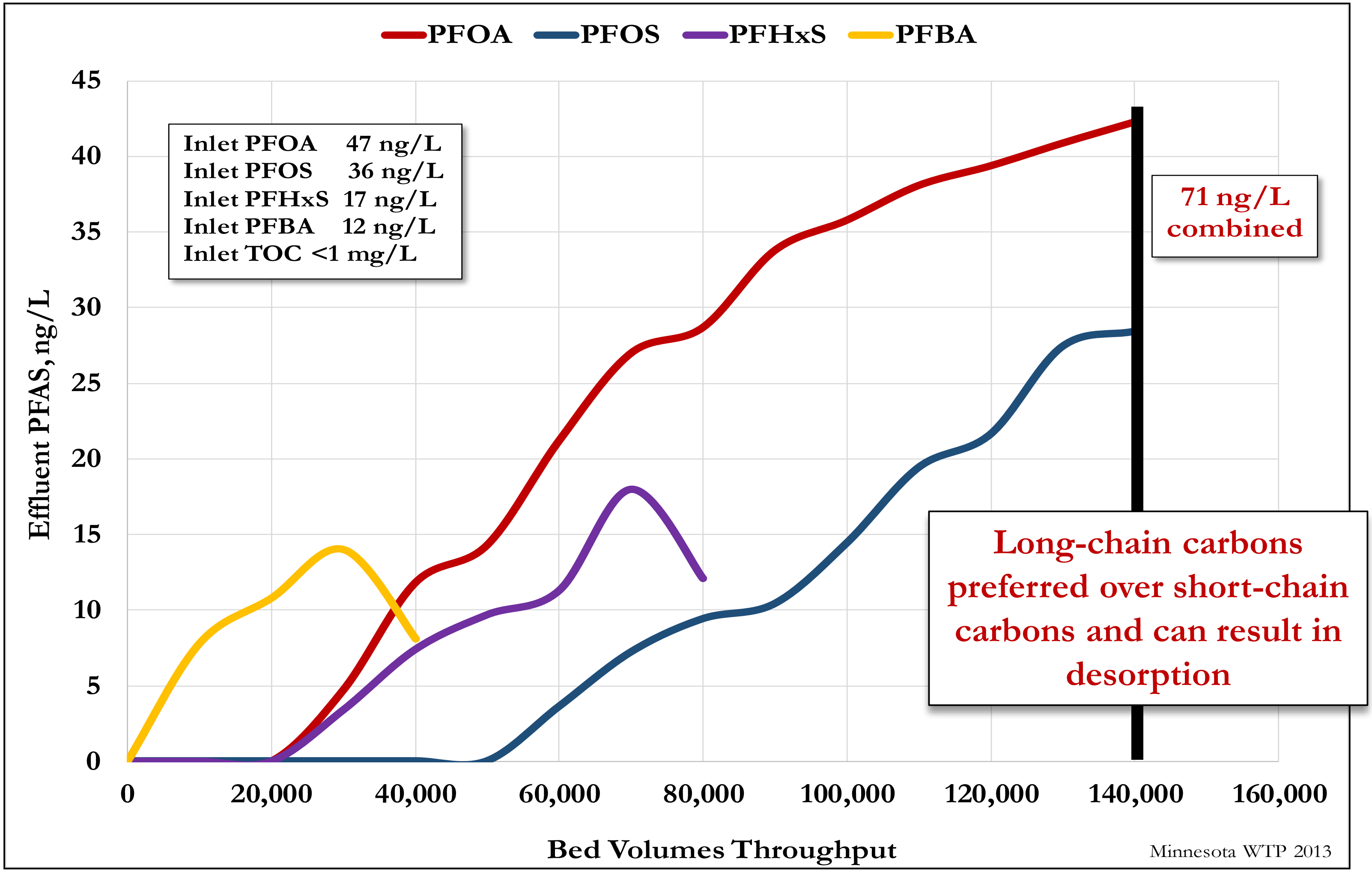

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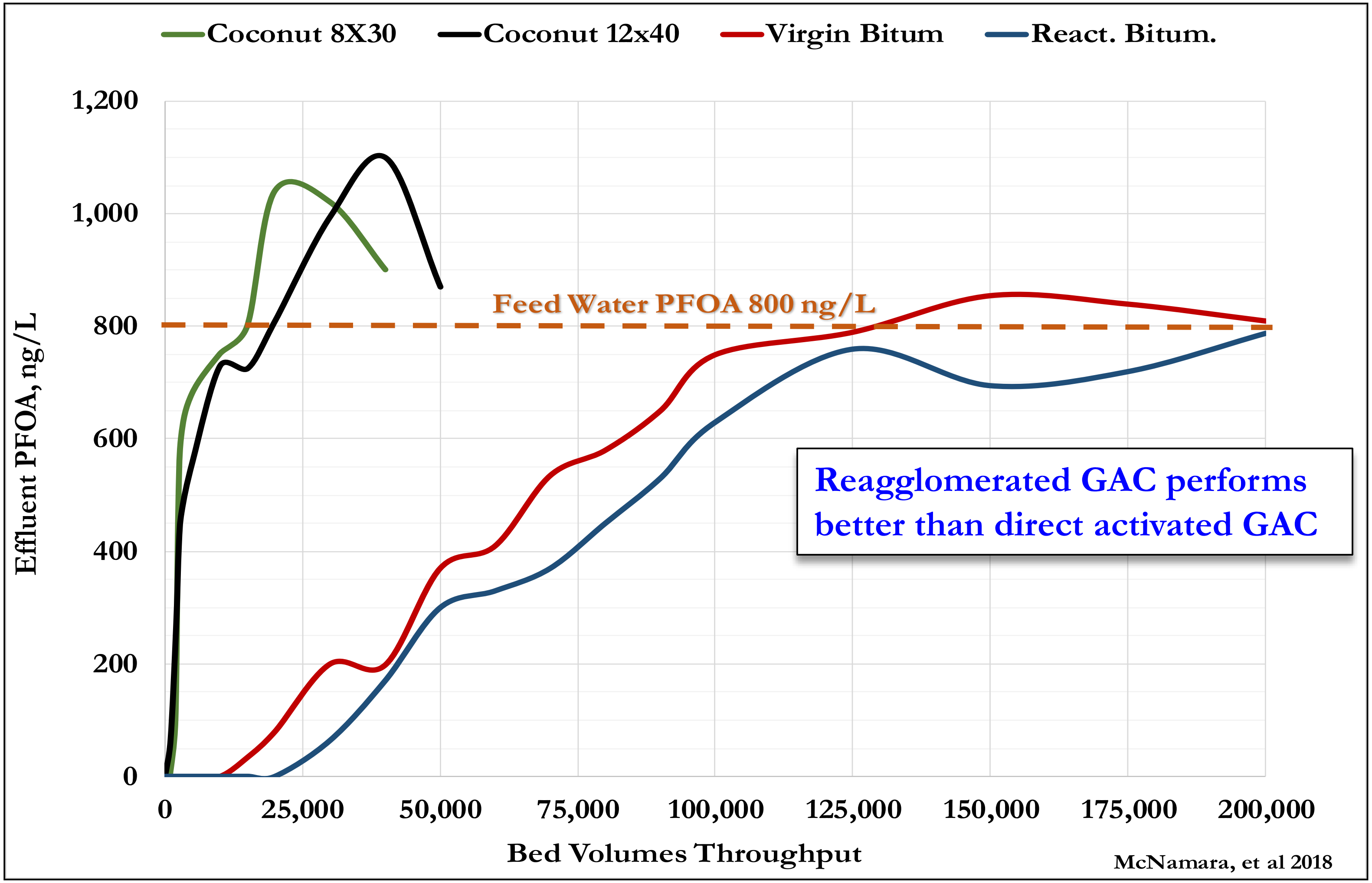

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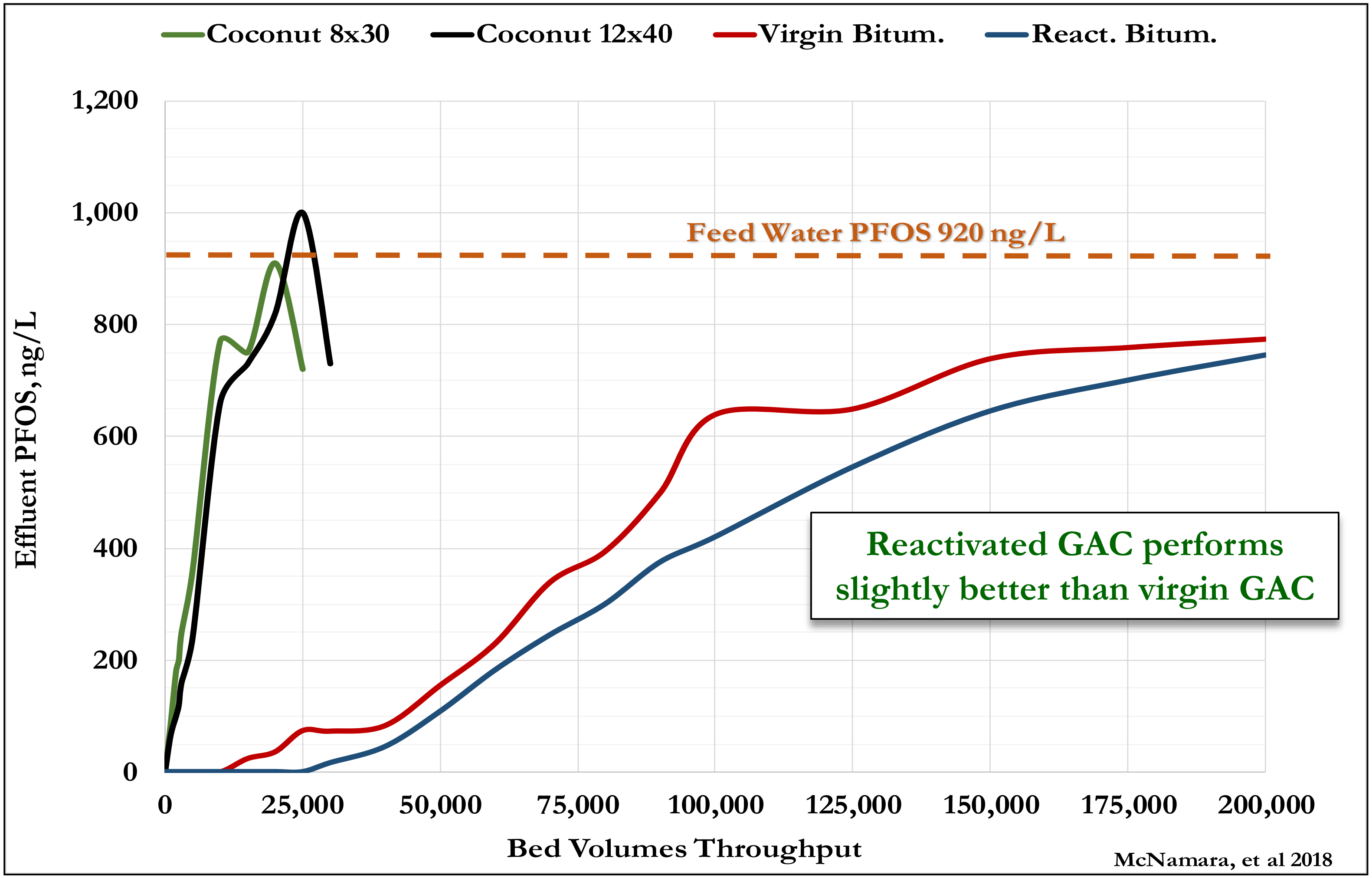

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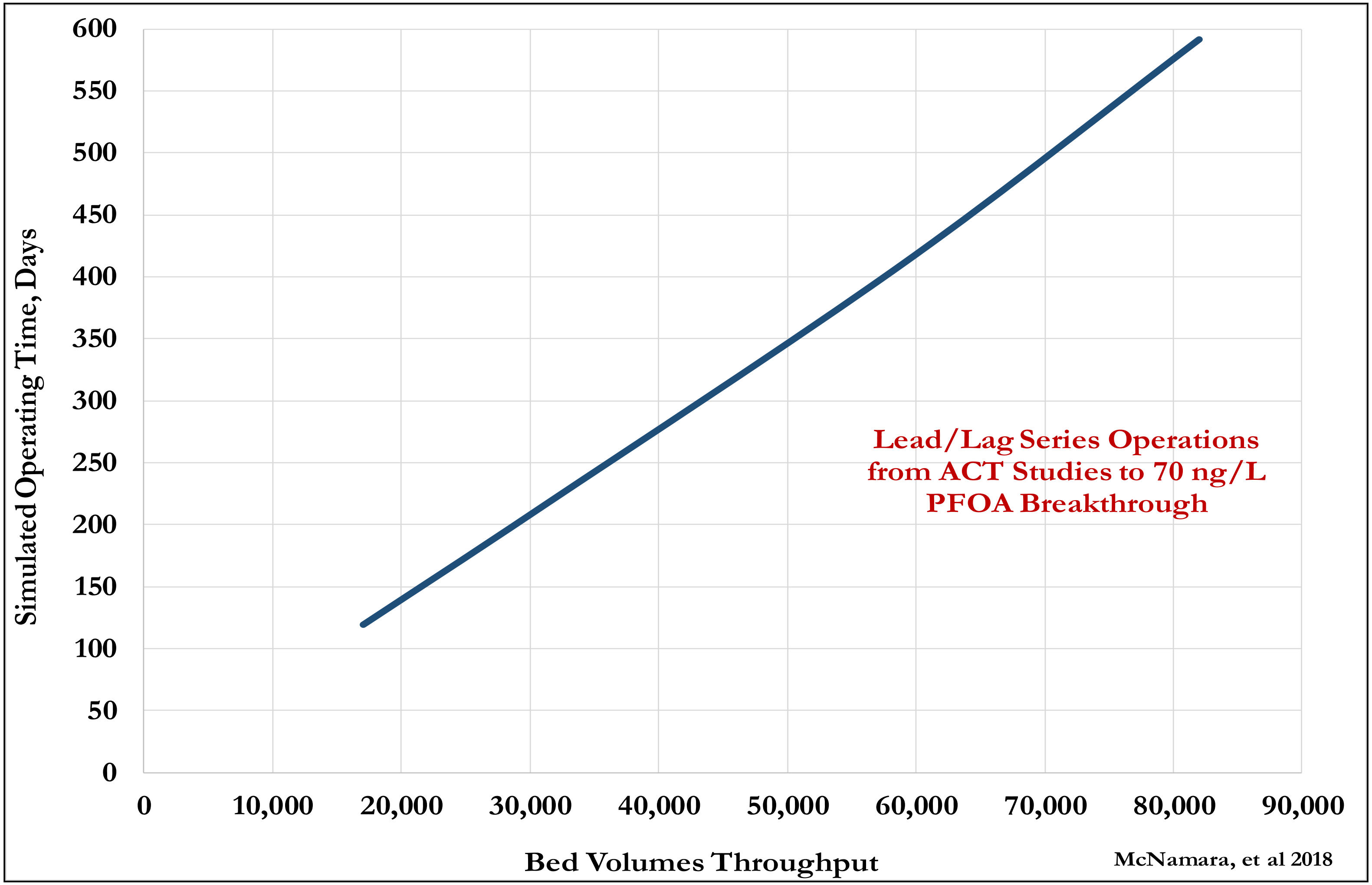

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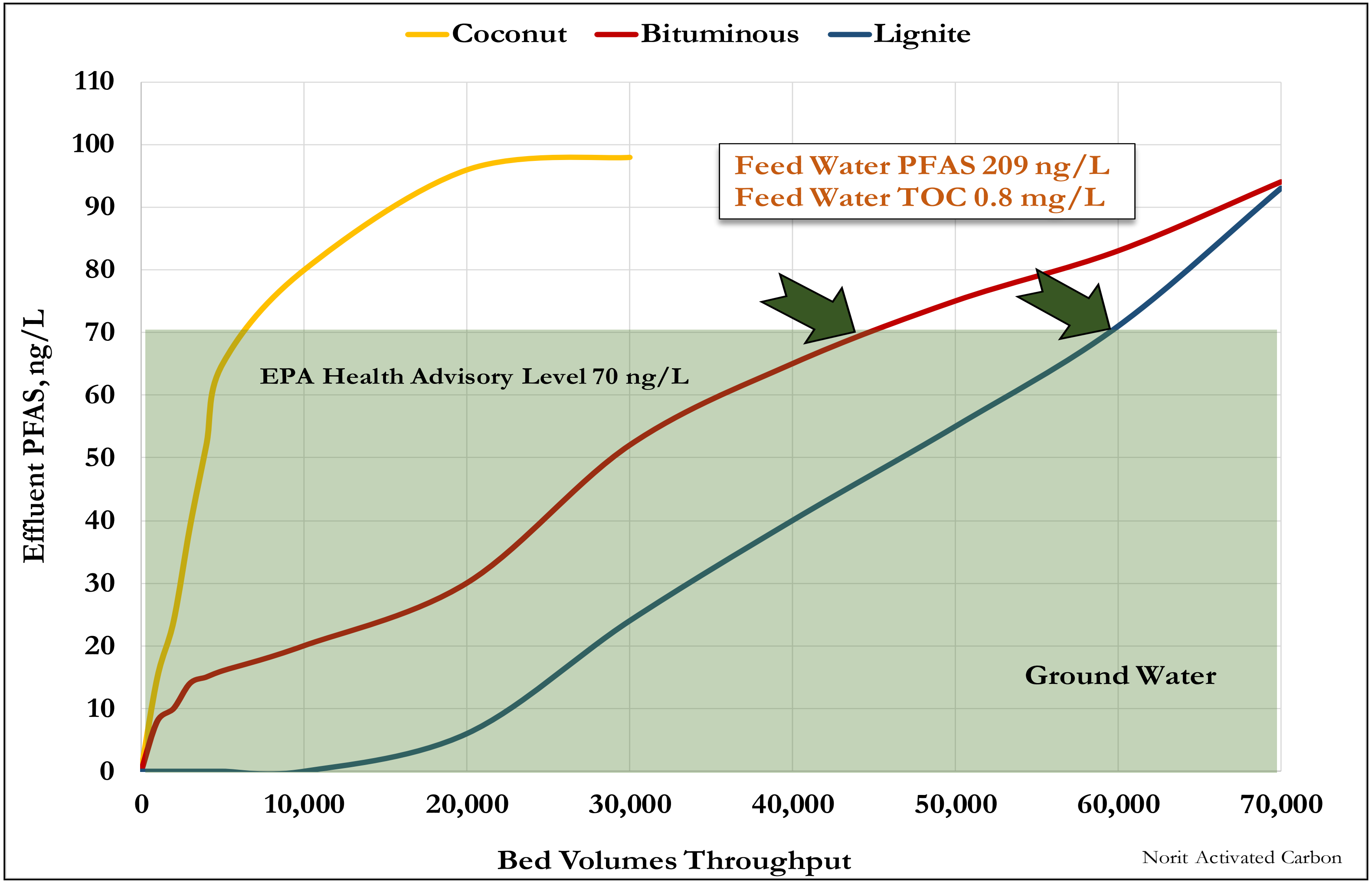

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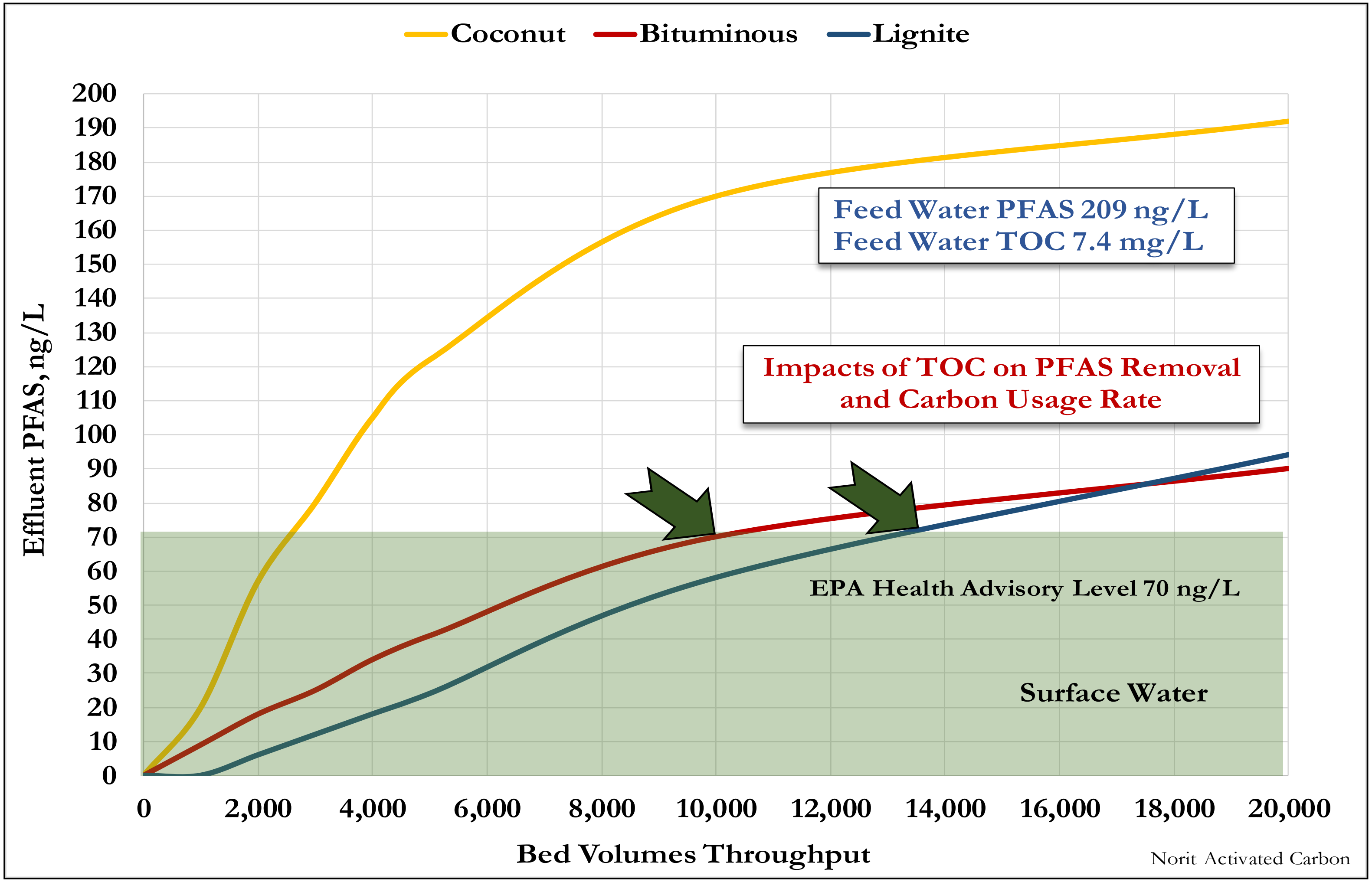

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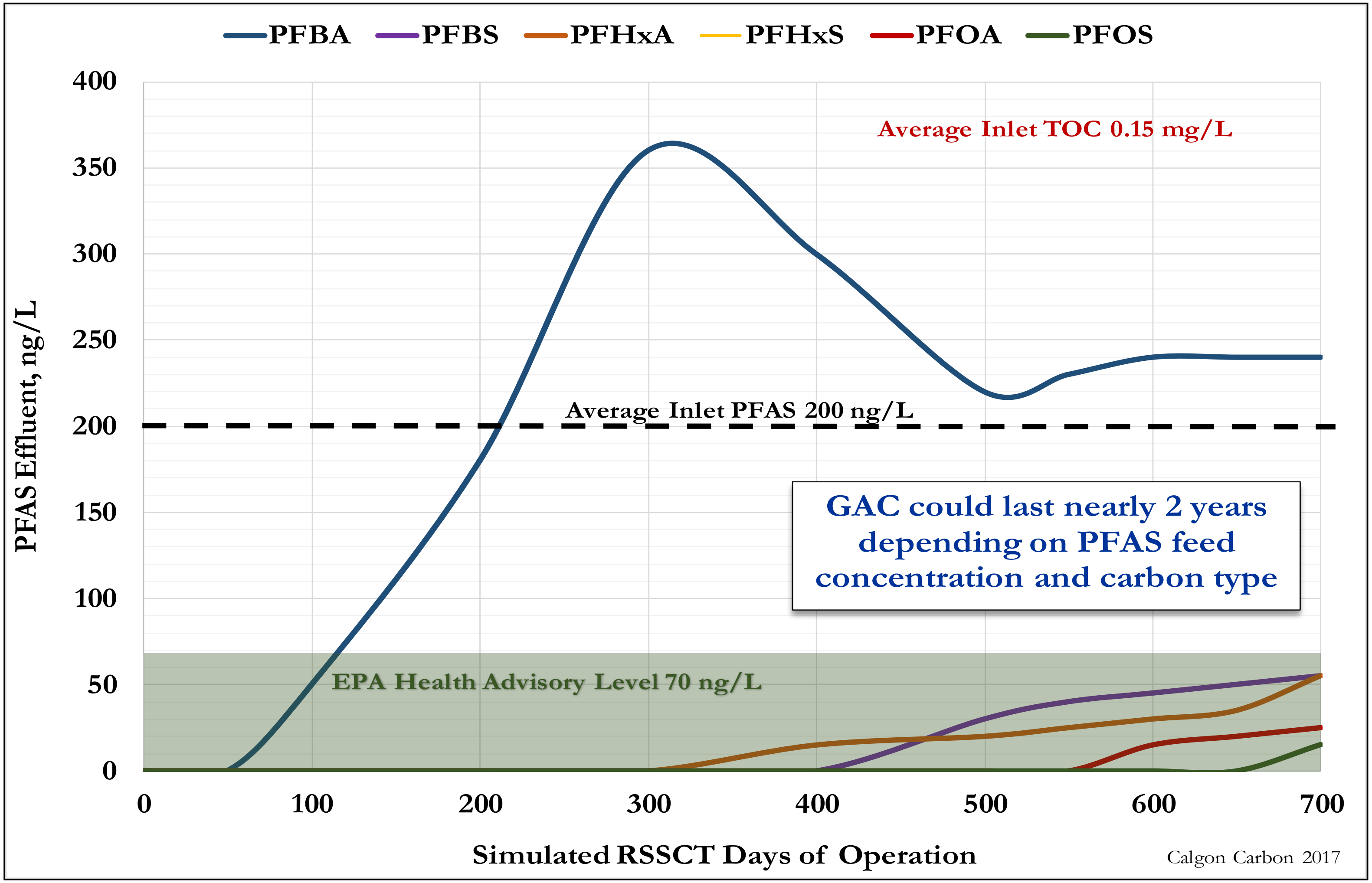

GAC Adsorption

- GAC Reactivation Process
  - Occurs at very high temperatures (1,800°C)
    - PFOA destroyed 662°C
    - PFOS destroyed 1,112°C
  - Excess water and PFAS desorbs from GAC releasing F^- ion
  - Fluoride ion combusts in kiln combining with hydrogen (HF)
  - HF destroyed in kiln operations
  - Oxidizer/afterburner destroys organics, neutralizes acid gases, and captures particulates
  - Off-gas verified by stack emissions testing
- PFAS is not returned to the GAC or to the environment
  - Most environmentally friendly PFAS removal process

Summary

- Complex treatments can be made simple
- Side stream treatment may be sufficient in some plants
  - Depending on feed water PFAS
- AEX and RO waste streams need treatment or proper disposal methods
- GAC reactivation destroys PFAS
  - Can improve adsorption versus virgin GAC
- Hybrid (mixed) systems show promise for high PFAS levels
  - Reduces waste stream PFAS content
  - Can be side stream AEX/RO and blend GAC effluent depending on treatment needs

Questions

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