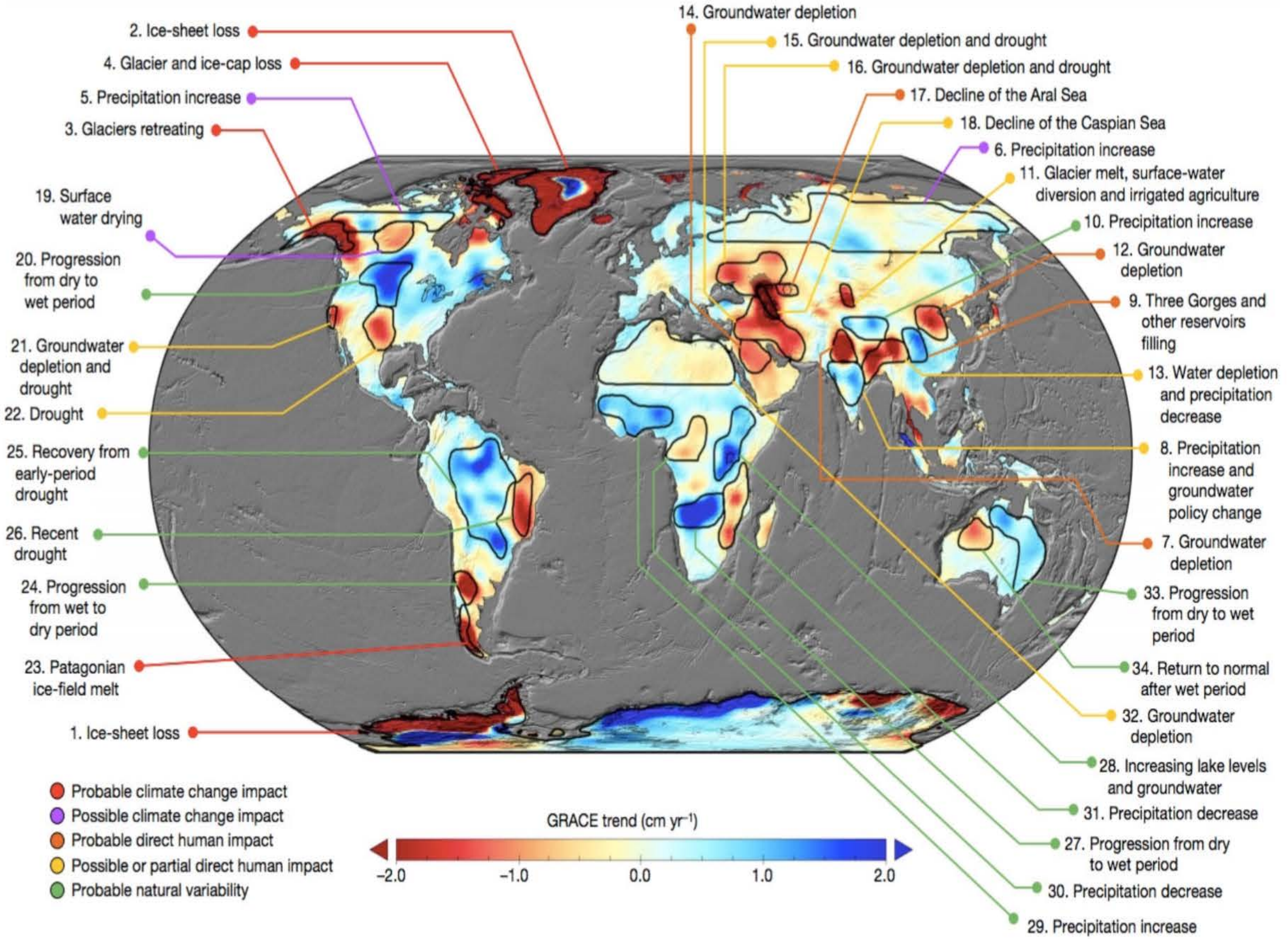
Emerging Chemicals in Groundwater: Perils and Challenges

Jane Williams, Executive Director
California Communities Against Toxics
October 11, 2018

"Our future challenges could not be more clear from looking at this map."

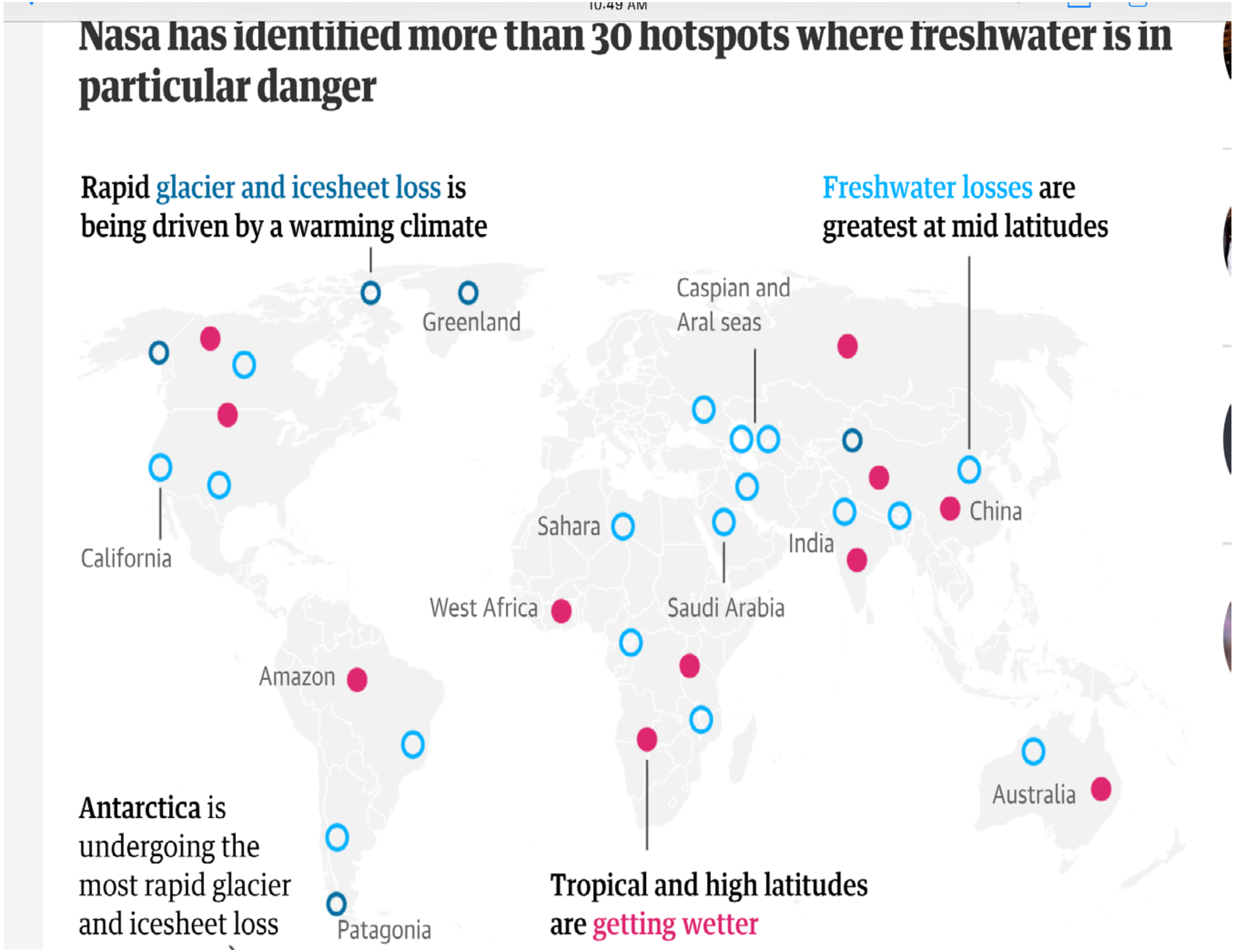
Global Problems:

Groundwater Contamination is now one of them.



Rodell et al, 2018

NASA Identifies California As a Place Where Freshwater is in Danger.



Nasa has identified more than 30 hotspots where freshwater is in particular danger

Rapid glacier and icesheet loss is being driven by a warming climate

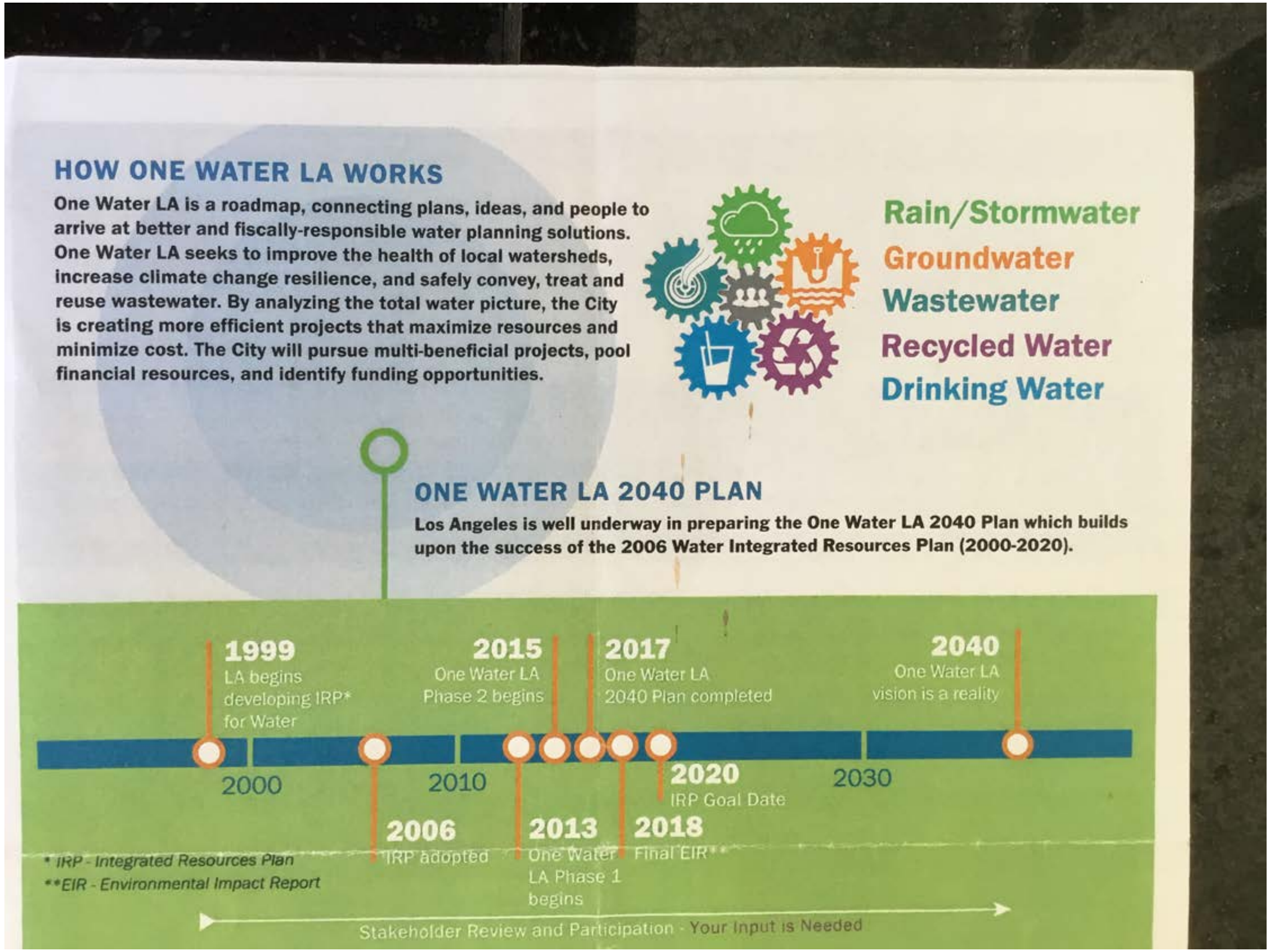
Freshwater losses are greatest at mid latitudes

Antarctica is undergoing the most rapid glacier and icesheet loss

Tropical and high latitudes are getting wetter

One Water LA: Potential Public Health Disaster.

Let’s see why…



HOW ONE WATER LA WORKS

One Water LA is a roadmap, connecting plans, ideas, and people to arrive at better and fiscally-responsible water planning solutions. One Water LA seeks to improve the health of local watersheds, increase climate change resilience, and safely convey, treat and reuse wastewater. By analyzing the total water picture, the City is creating more efficient projects that maximize resources and minimize cost. The City will pursue multi-beneficial projects, pool financial resources, and identify funding opportunities.

Rain/Stormwater
Groundwater
Wastewater
Recycled Water
Drinking Water

ONE WATER LA 2040 PLAN

Los Angeles is well underway in preparing the One Water LA 2040 Plan which builds upon the success of the 2006 Water Integrated Resources Plan (2000-2020).

1999 LA begins developing IRP* for Water

2006 IRP adopted

2013 One Water LA Phase 1 begins

2015 One Water LA Phase 2 begins

2017 One Water LA 2040 Plan completed

2018 Final EIR**

2020 IRP Goal Date

2040 One Water LA vision is a reality

** IRP - Integrated Resources Plan*
***EIR - Environmental Impact Report*

Stakeholder Review and Participation - Your Input is Needed

What are Emerging Contaminants?

- Over 100 chemicals are on the USEPA CCL 4 list:

- Chemicals that disrupt the endocrine system
- Pharmaceuticals
- Solvents
- Flame retardants
- Pesticides
- Herbicides
- Many more

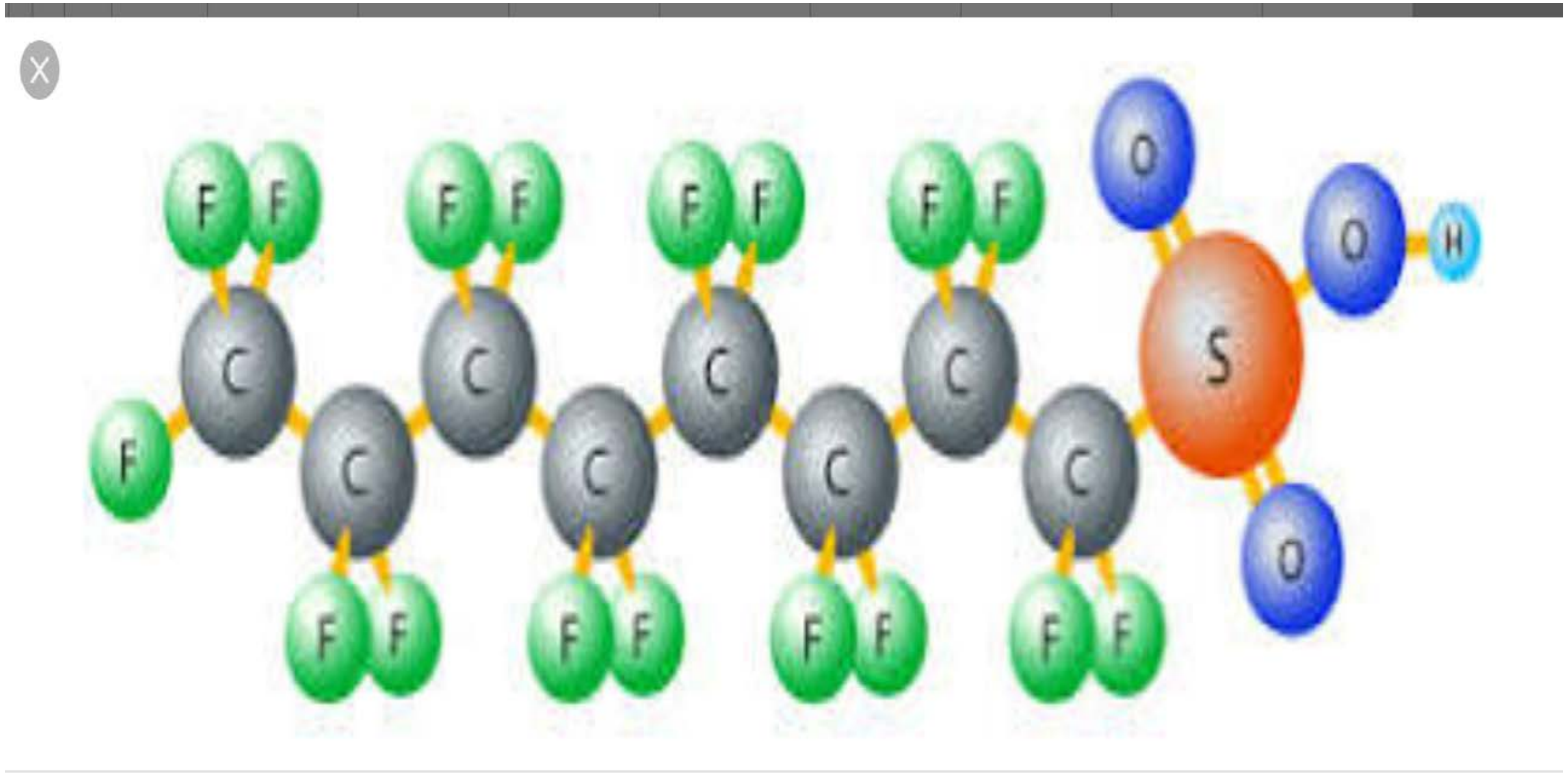
How are Chemicals on the CCL 4 list identified?

- **The Contaminant Candidate List (CCL) is a list of contaminants that are currently not subject to any proposed or promulgated national primary drinking water regulations, but are known or anticipated to occur in public water systems.**

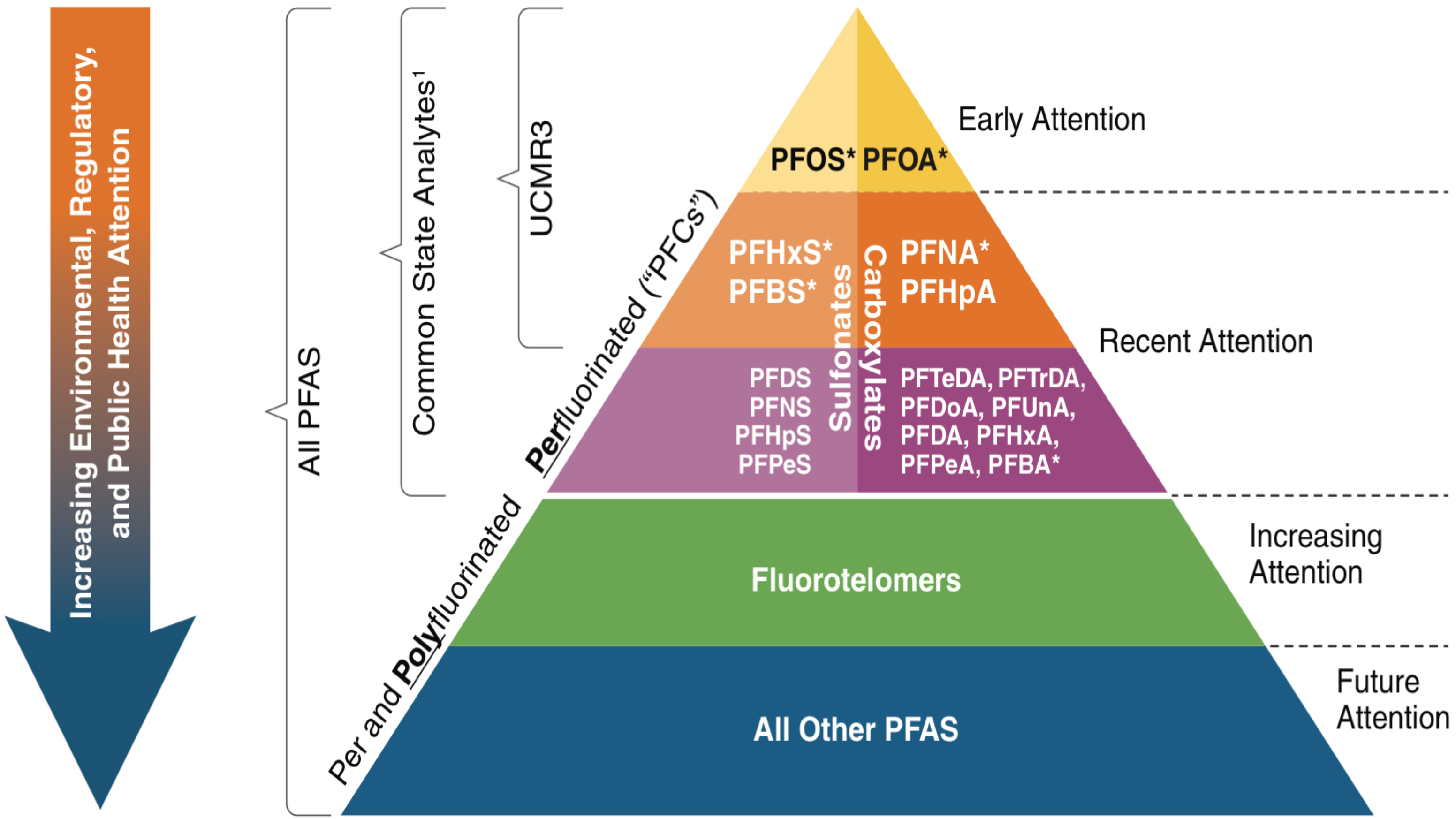
What is the state regulating and at what levels?

- As our ability to measure smaller amounts of chemicals in the environment expands we can see the impacts of low dose exposure on public health much better.
- The last two regulatory levels set by the state have been in the low parts per trillion.
- The health impacts we measure are alarming: carcinogenicity, immune systems impacts, neurotoxicity, and damaged kidneys to name a few.

PFAS Chemicals: The Forever Chemicals



The Graphic of Emerging Awareness



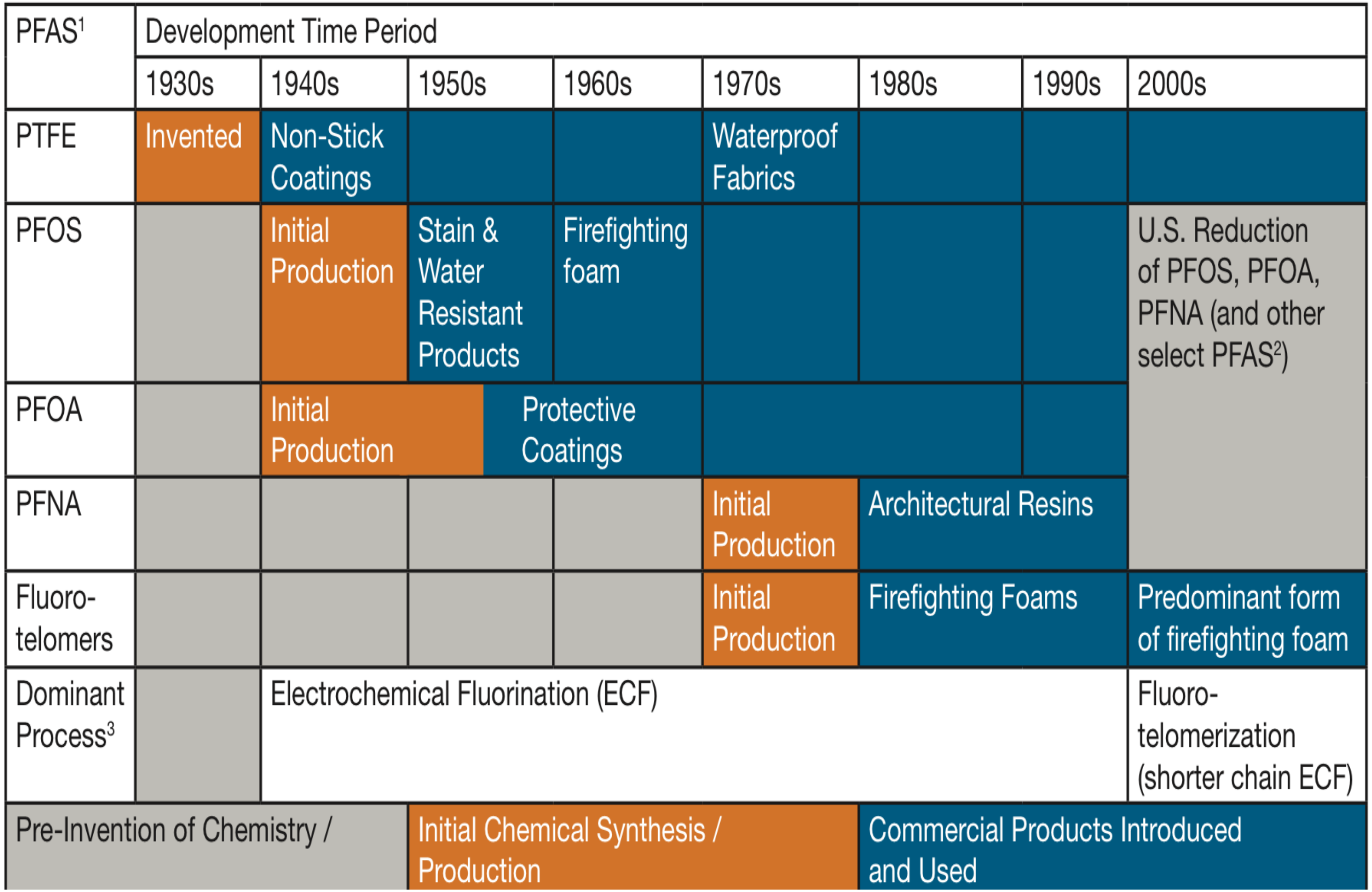
*Common regulatory criteria or health advisories
[1] Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

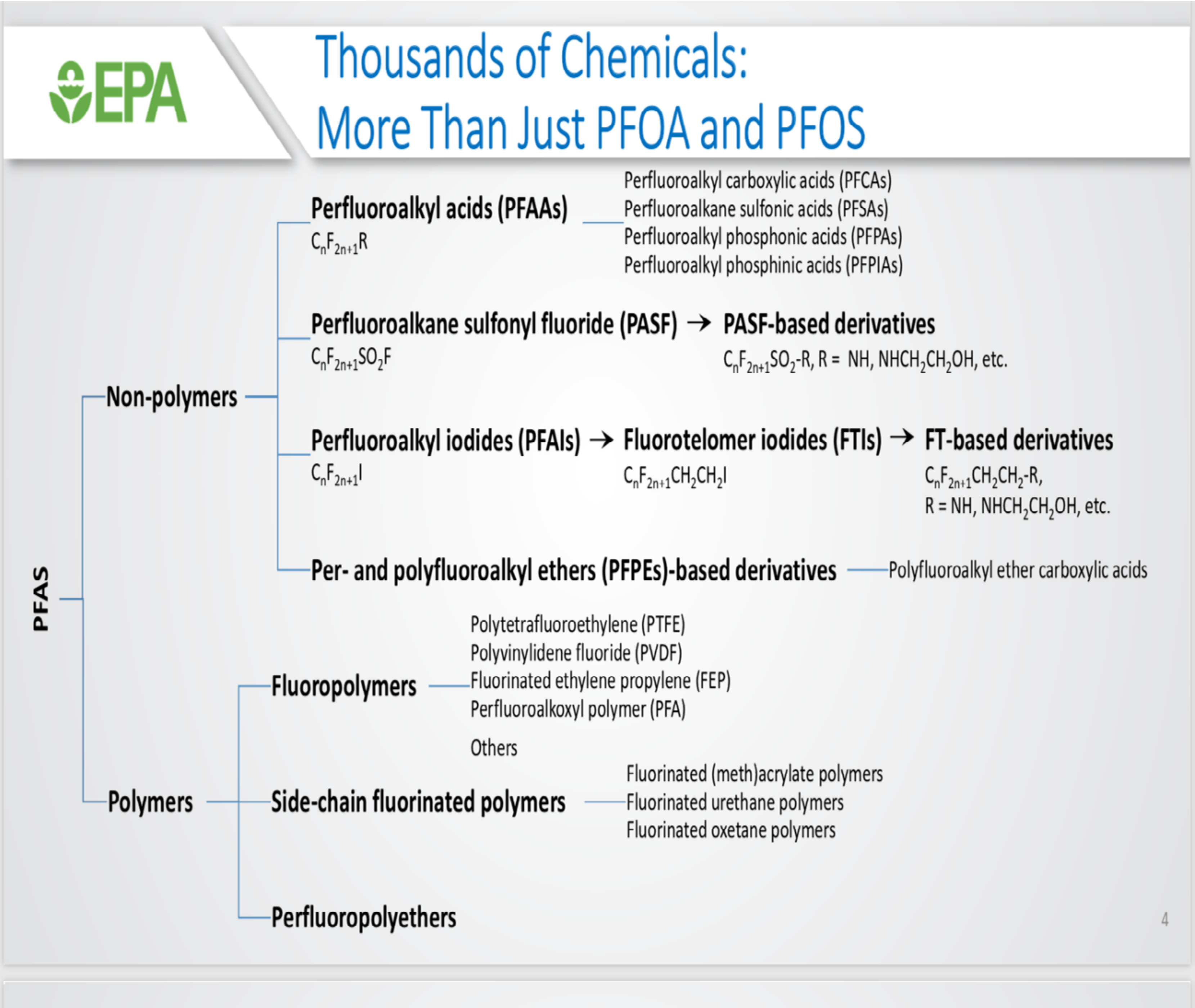
These chemicals have been made since the 1940s.

Table 2-1. Discovery and manufacturing history of select PFAS



PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

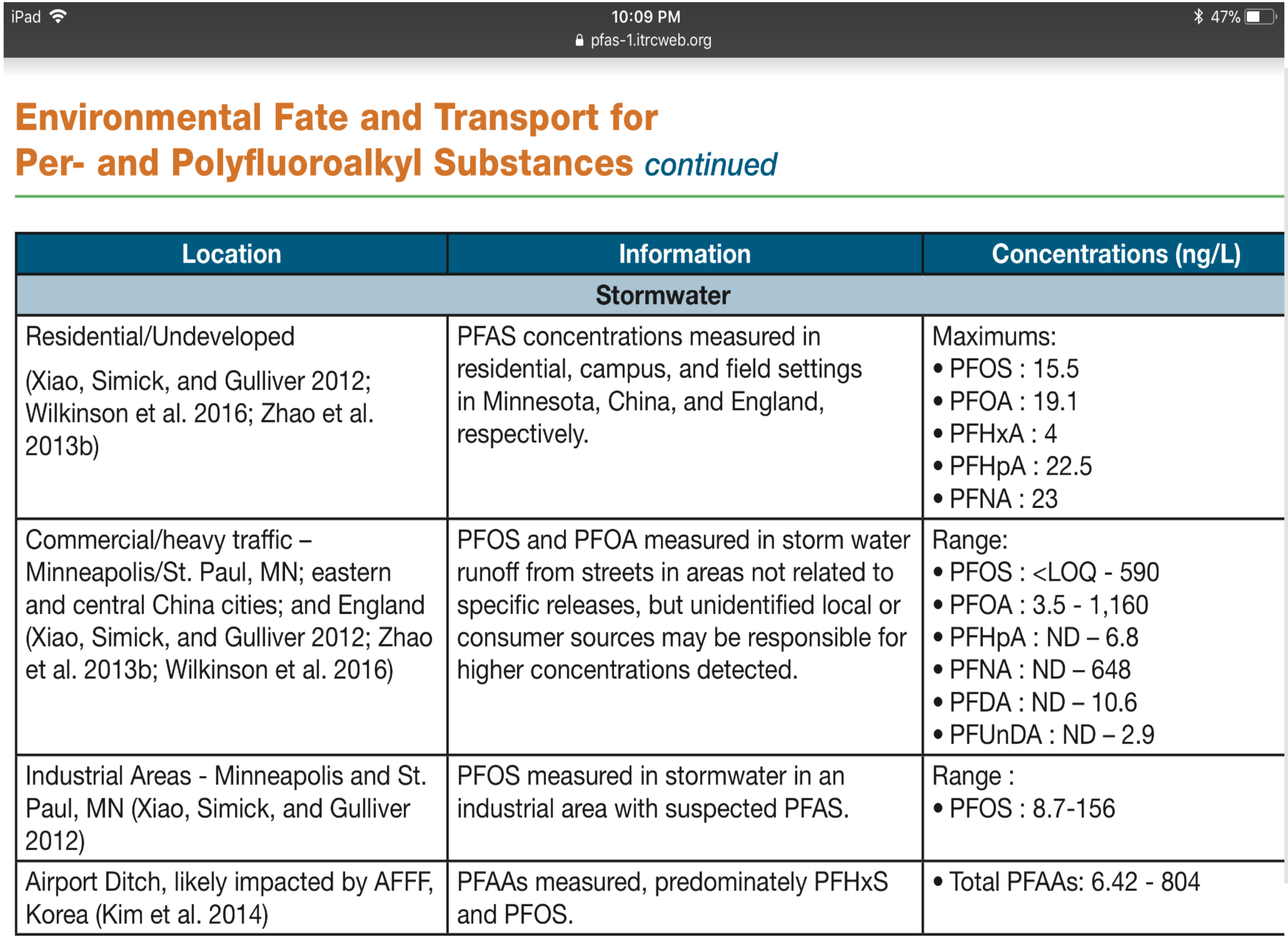
PFAS Chemicals Encompass a Large Chemical Family.



Thousands of Chemicals: More Than Just PFOA and PFOS

PFAS
- **Non-polymers**
  - **Perfluoroalkyl acids (PFAAs)** $C_nF_{2n+1}R$
    - Perfluoroalkyl carboxylic acids (PFCAs)
    - Perfluoroalkane sulfonic acids (PFSAs)
    - Perfluoroalkyl phosphonic acids (PFPAs)
    - Perfluoroalkyl phosphinic acids (PFPIAs)
  - **Perfluoroalkane sulfonyl fluoride (PASF)** $C_nF_{2n+1}SO_2F$ → **PASF-based derivatives** $C_nF_{2n+1}SO_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **Fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
  - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
    - Polyfluoroalkyl ether carboxylic acids
- **Polymers**
  - **Fluoropolymers**
    - Polytetrafluoroethylene (PTFE)
    - Polyvinylidene fluoride (PVDF)
    - Fluorinated ethylene propylene (FEP)
    - Perfluoroalkoxyl polymer (PFA)
    - Others
  - **Side-chain fluorinated polymers**
    - Fluorinated (meth)acrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers
  - **Perfluoropolyethers**

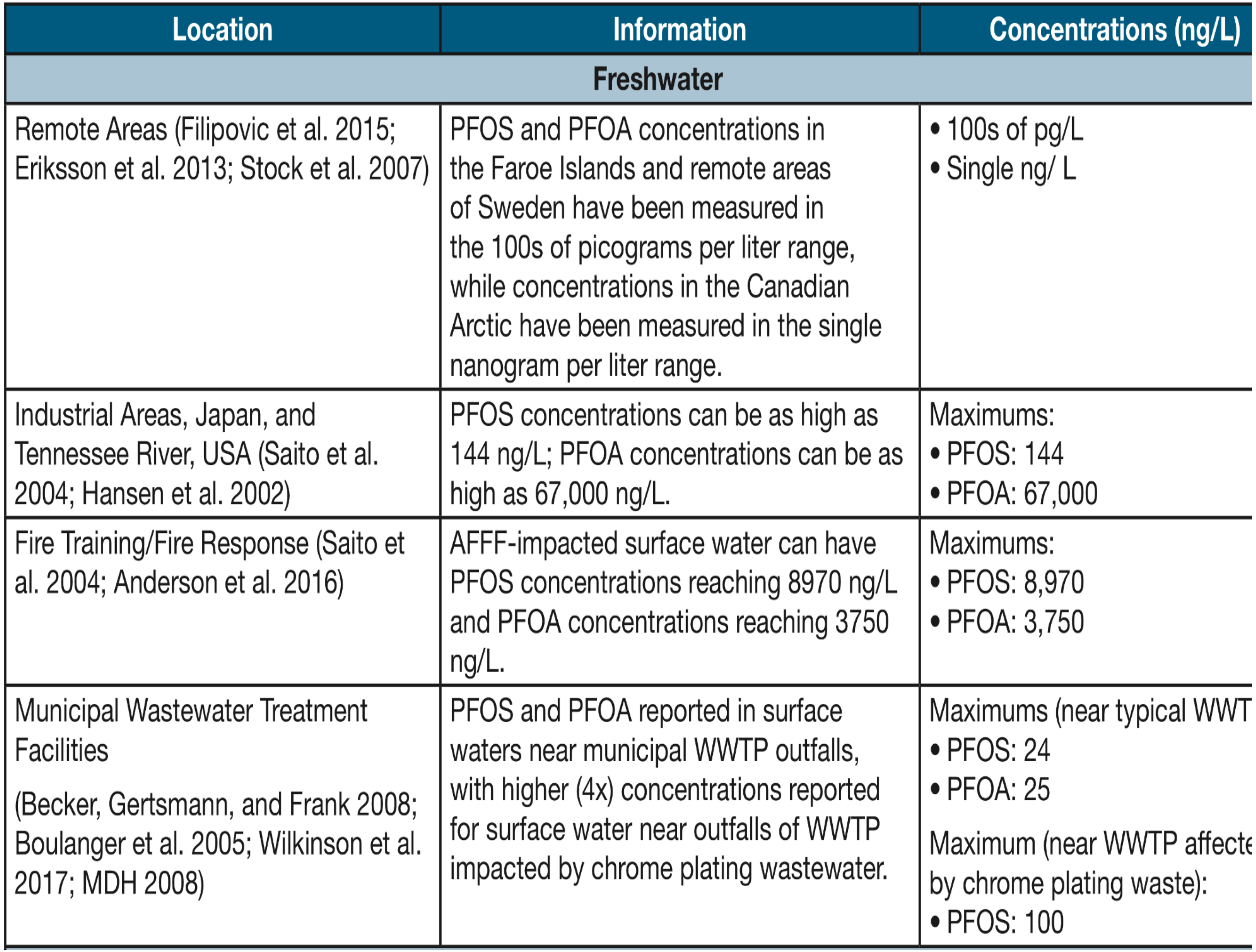
PFAS chemicals are now a ubiquitous pollutant in stormwater.



Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances *continued*

Location	Information	Concentrations (ng/L)
Stormwater		
Residential/Undeveloped (Xiao, Simick, and Gulliver 2012; Wilkinson et al. 2016; Zhao et al. 2013b)	PFAS concentrations measured in residential, campus, and field settings in Minnesota, China, and England, respectively.	Maximums: • PFOS : 15.5 • PFOA : 19.1 • PFHxA : 4 • PFHpA : 22.5 • PFNA : 23
Commercial/heavy traffic – Minneapolis/St. Paul, MN; eastern and central China cities; and England (Xiao, Simick, and Gulliver 2012; Zhao et al. 2013b; Wilkinson et al. 2016)	PFOS and PFOA measured in storm water runoff from streets in areas not related to specific releases, but unidentified local or consumer sources may be responsible for higher concentrations detected.	Range: • PFOS : <LOQ - 590 • PFOA : 3.5 - 1,160 • PFHpA : ND – 6.8 • PFNA : ND – 648 • PFDA : ND – 10.6 • PFUnDA : ND – 2.9
Industrial Areas - Minneapolis and St. Paul, MN (Xiao, Simick, and Gulliver 2012)	PFOS measured in stormwater in an industrial area with suspected PFAS.	Range : • PFOS : 8.7-156
Airport Ditch, likely impacted by AFFF, Korea (Kim et al. 2014)	PFAAs measured, predominately PFHxS and PFOS.	• Total PFAAs: 6.42 - 804

PFAS Chemicals are ubiquitous in fresh water resources globally.



Location	Information	Concentrations (ng/L)
Freshwater		
Remote Areas (Filipovic et al. 2015; Eriksson et al. 2013; Stock et al. 2007)	PFOS and PFOA concentrations in the Faroe Islands and remote areas of Sweden have been measured in the 100s of picograms per liter range, while concentrations in the Canadian Arctic have been measured in the single nanogram per liter range.	• 100s of pg/L • Single ng/ L
Industrial Areas, Japan, and Tennessee River, USA (Saito et al. 2004; Hansen et al. 2002)	PFOS concentrations can be as high as 144 ng/L; PFOA concentrations can be as high as 67,000 ng/L.	Maximums: • PFOS: 144 • PFOA: 67,000
Fire Training/Fire Response (Saito et al. 2004; Anderson et al. 2016)	AFFF-impacted surface water can have PFOS concentrations reaching 8970 ng/L and PFOA concentrations reaching 3750 ng/L.	Maximums: • PFOS: 8,970 • PFOA: 3,750
Municipal Wastewater Treatment Facilities (Becker, Gertsmann, and Frank 2008; Boulanger et al. 2005; Wilkinson et al. 2017; MDH 2008)	PFOS and PFOA reported in surface waters near municipal WWTP outfalls, with higher (4x) concentrations reported for surface water near outfalls of WWTP impacted by chrome plating wastewater.	Maximums (near typical WWT • PFOS: 24 • PFOA: 25 Maximum (near WWTP affecte by chrome plating waste): • PFOS: 100

What these Chemicals used for?

Reported uses of PFCs and PFC products

Wide range of uses

- AFFF agents / surfactants / surface protectants
- Manufacture of fluoropolymers
- Raw material for surface treatment agent
- Anti reflective coatings (ARCs) for photolithography processes
- Coatings / additives
- Etchants for Aluminium Surface active agents
- Gaskets / seals / membranes / cable insulations
- Tubing / pipe liners / cable insulation
- Impregnation of glass or plastic
- Ion Exchange
- Lubricants
- Water/oil repellent
- Treatment of industrial stream

Major Known PFAS Sources:

Landfills
Chrome Platers
Fire fighting Foam
Wastewater Plants

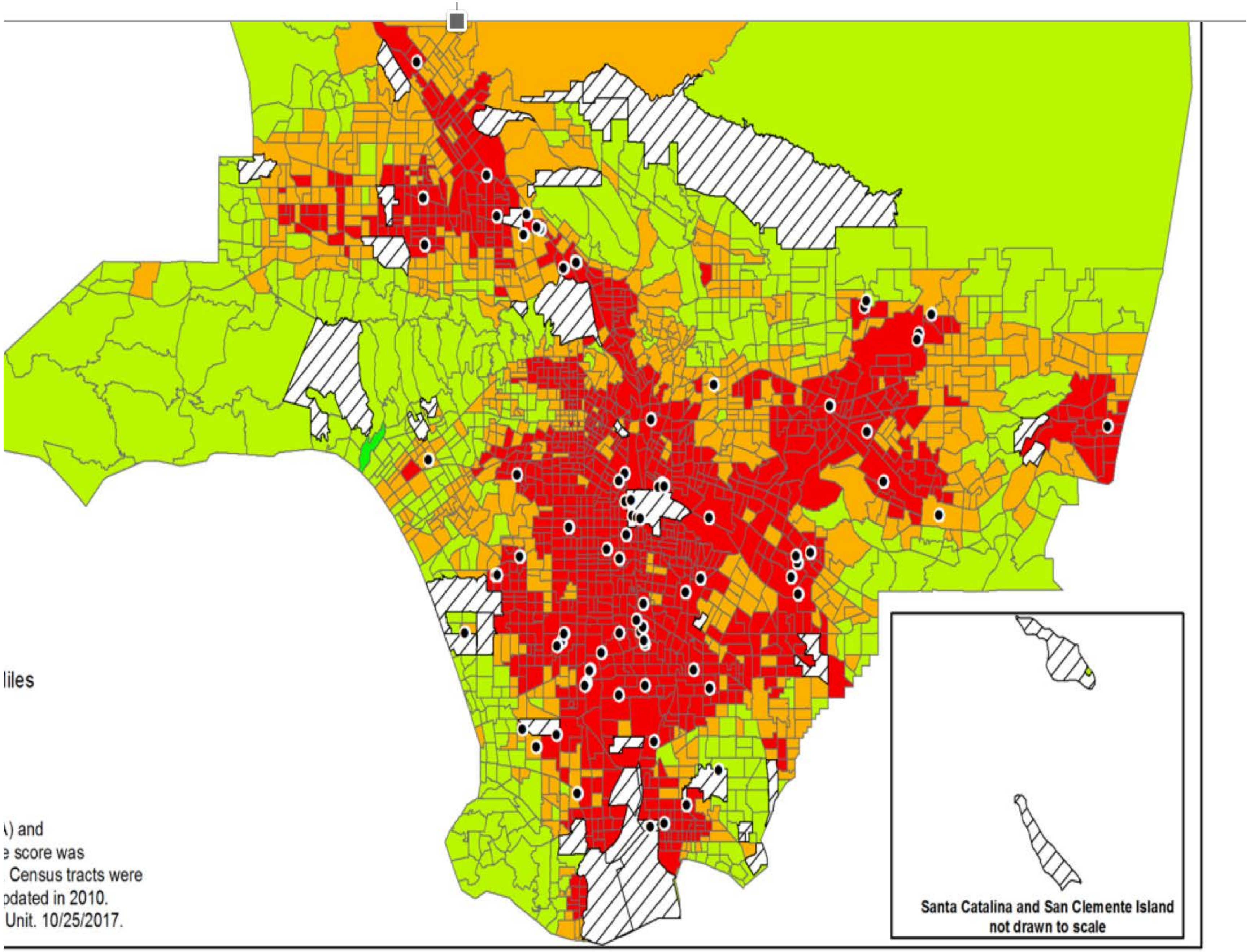
EPA Sources of PFAS in the Environment

- Direct release of PFAS or PFAS products into the environment
  - Use of aqueous film forming foam (AFFF) in training and emergency response
  - Release from industrial facility
- Chrome plating and etching facilities
- Landfills and leachates from disposal of consumer and industrial products containing PFAS
- Wastewater treatment effluent and land application of biosolids

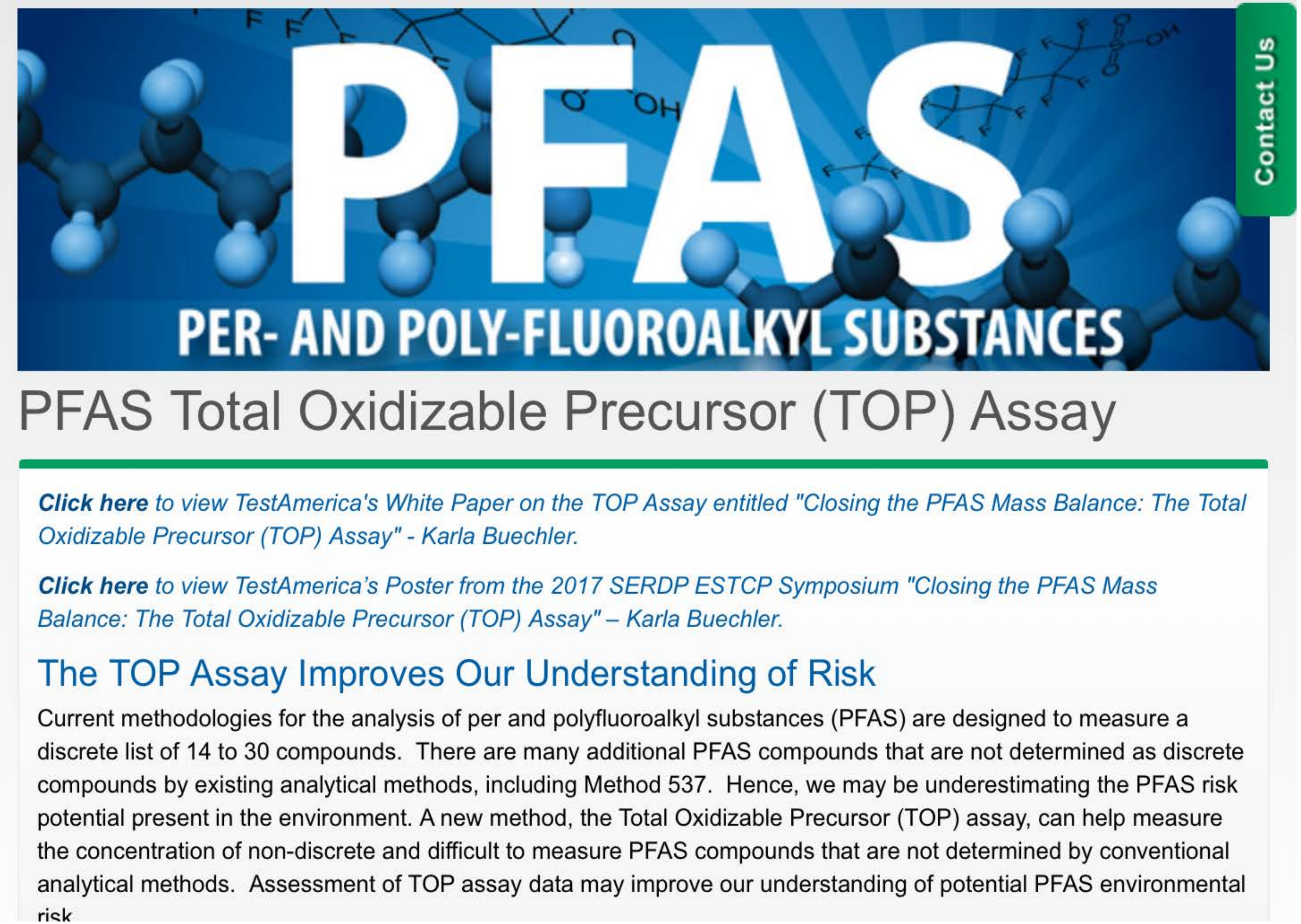
EPA Reasons for Concern

- Known or suspected toxicity
- PFAS and/or breakdown products are persistent in the environment

Chrome Platers in Los Angeles Are a Suspected Source of Contamination



How we test for PFAS Chemicals Makes a BIG Difference In What We SEE.



PFAS Total Oxidizable Precursor (TOP) Assay

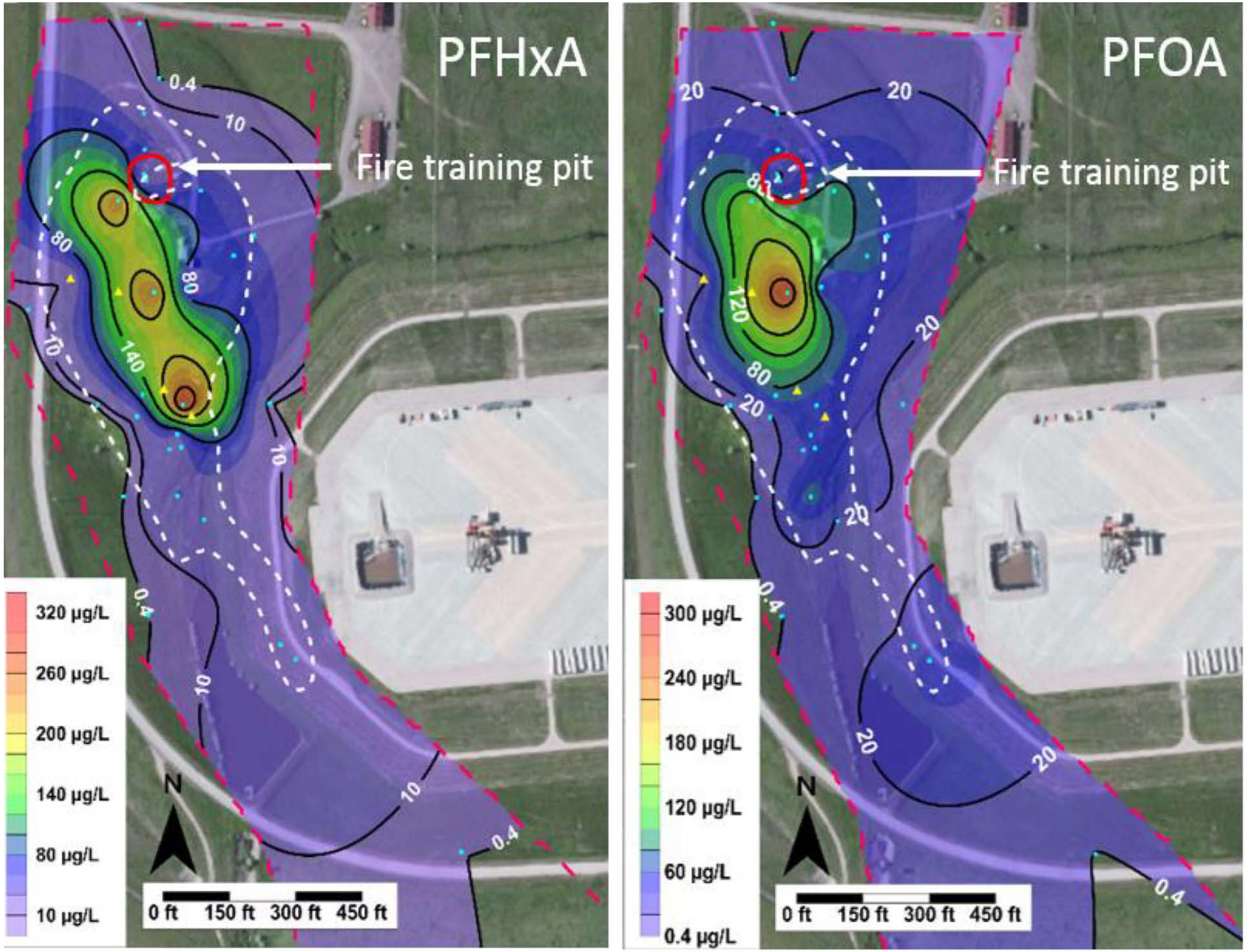
***Click here** to view TestAmerica's White Paper on the TOP Assay entitled "Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay" - Karla Buechler.*

***Click here** to view TestAmerica's Poster from the 2017 SERDP ESTCP Symposium "Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay" – Karla Buechler.*

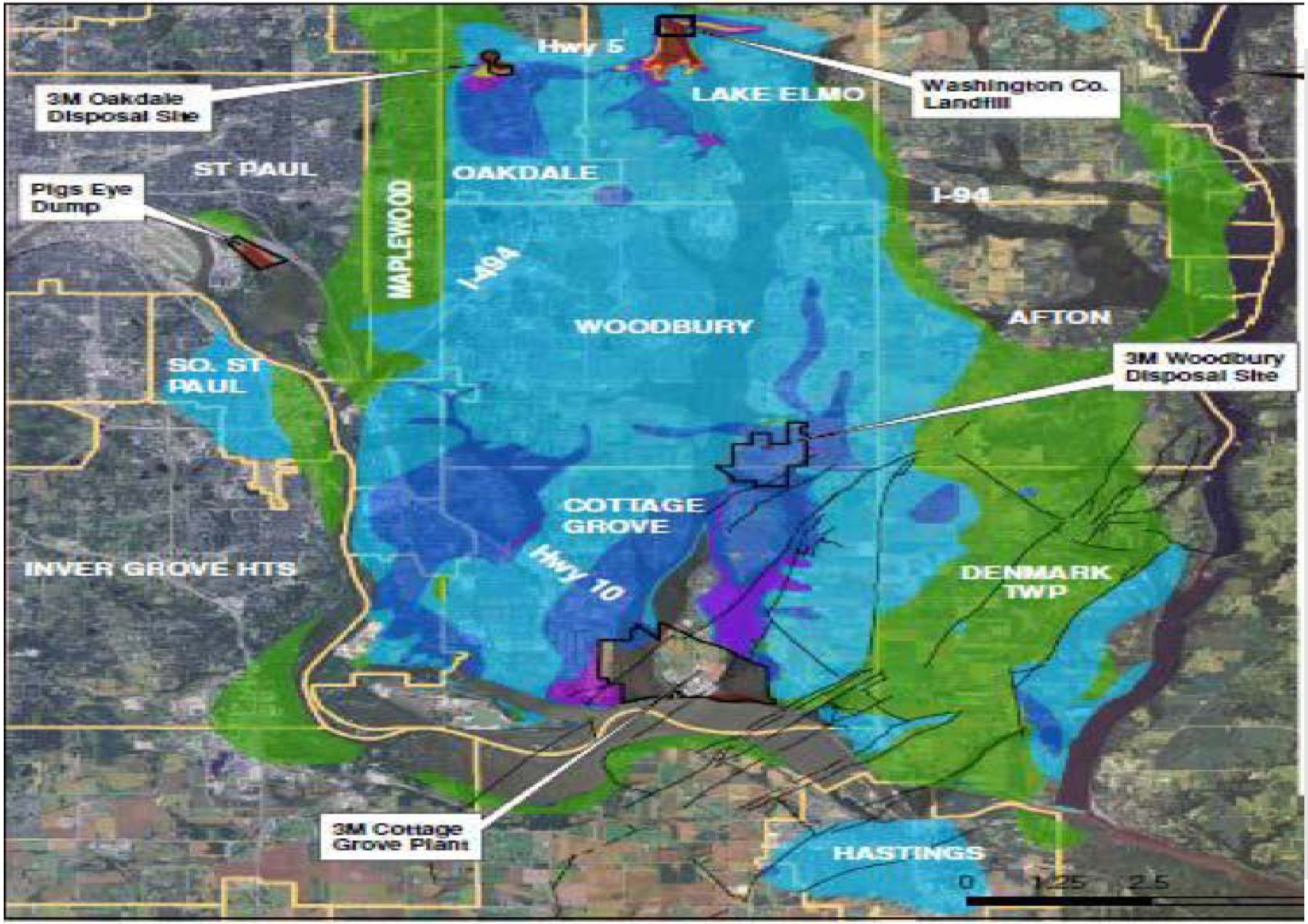
The TOP Assay Improves Our Understanding of Risk

Current methodologies for the analysis of per and polyfluoroalkyl substances (PFAS) are designed to measure a discrete list of 14 to 30 compounds. There are many additional PFAS compounds that are not determined as discrete compounds by existing analytical methods, including Method 537. Hence, we may be underestimating the PFAS risk potential present in the environment. A new method, the Total Oxidizable Precursor (TOP) assay, can help measure the concentration of non-discrete and difficult to measure PFAS compounds that are not determined by conventional analytical methods. Assessment of TOP assay data may improve our understanding of potential PFAS environmental risk.

PFAS Chemicals have Created HUGE Contamination Plumes many miles long.

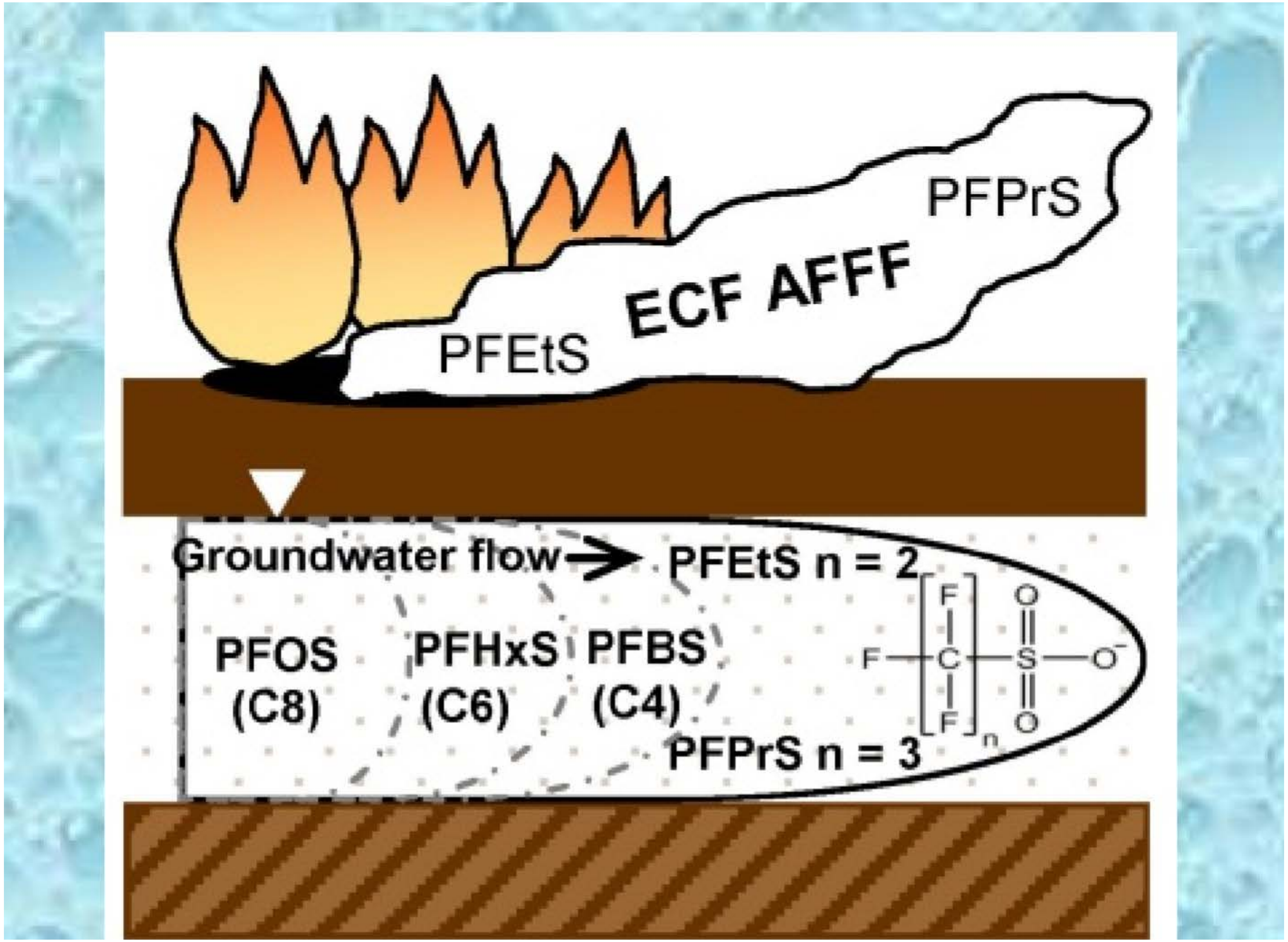


This plume in Minnesota is 100 square miles.



(MDH, 201

Shorter-chained PFAS Tend to Travel First in the Groundwater.



PFAS Chemicals Have Many Uses.

EPA

Used in Homes, Businesses & Industry

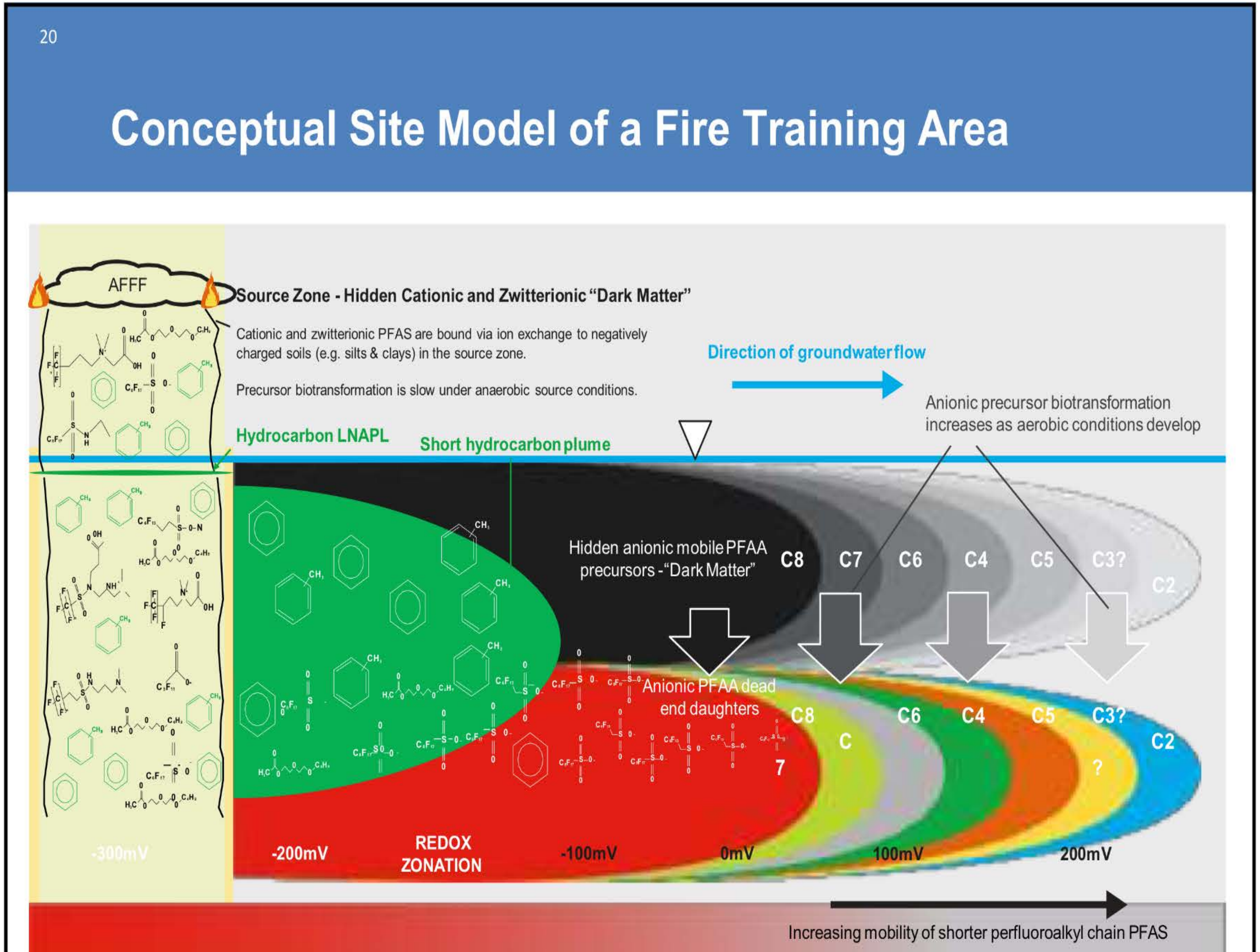
- Food contact surfaces such as cookware, pizza boxes, fast food wrappers, popcorn bags, etc.
- Polishes, waxes, and paints
- Stain repellants for carpets, clothing, upholstered furniture, etc.
- Cleaning products
- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals such as hydraulic fluid, fuel additives, etc.

What is Aqueous Film Forming Foam?

AFFF

A man walks through Aqueous Film-Forming Foam after a test of the sprinkler systems aboard the flight deck of the aircraft carrier USS Ronald Reagan, May 19, 2010. Photo: U.S. Navy

Conceptual Models of AFFF Sites show us what we should be looking for at the leading edges of the plumes.



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Conceptual Site Model of a Fire Training Area

Source Zone - Hidden Cationic and Zwitterionic "Dark Matter"

Cationic and zwitterionic PFAS are bound via ion exchange to negatively charged soils (e.g. silts & clays) in the source zone.

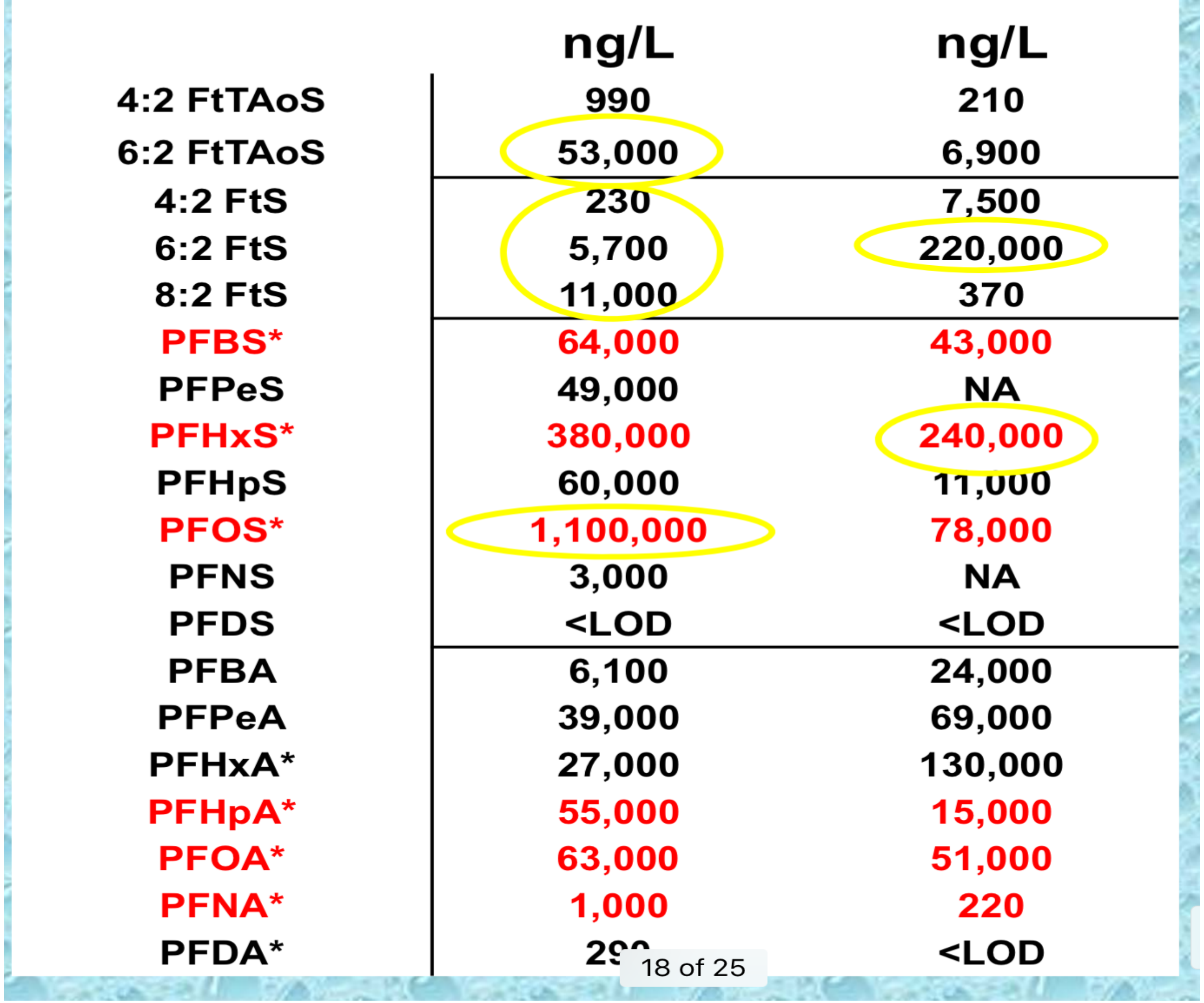
Precursor biotransformation is slow under anaerobic source conditions.

Anionic precursor biotransformation increases as aerobic conditions develop

Increasing mobility of shorter perfluoroalkyl chain PFAS

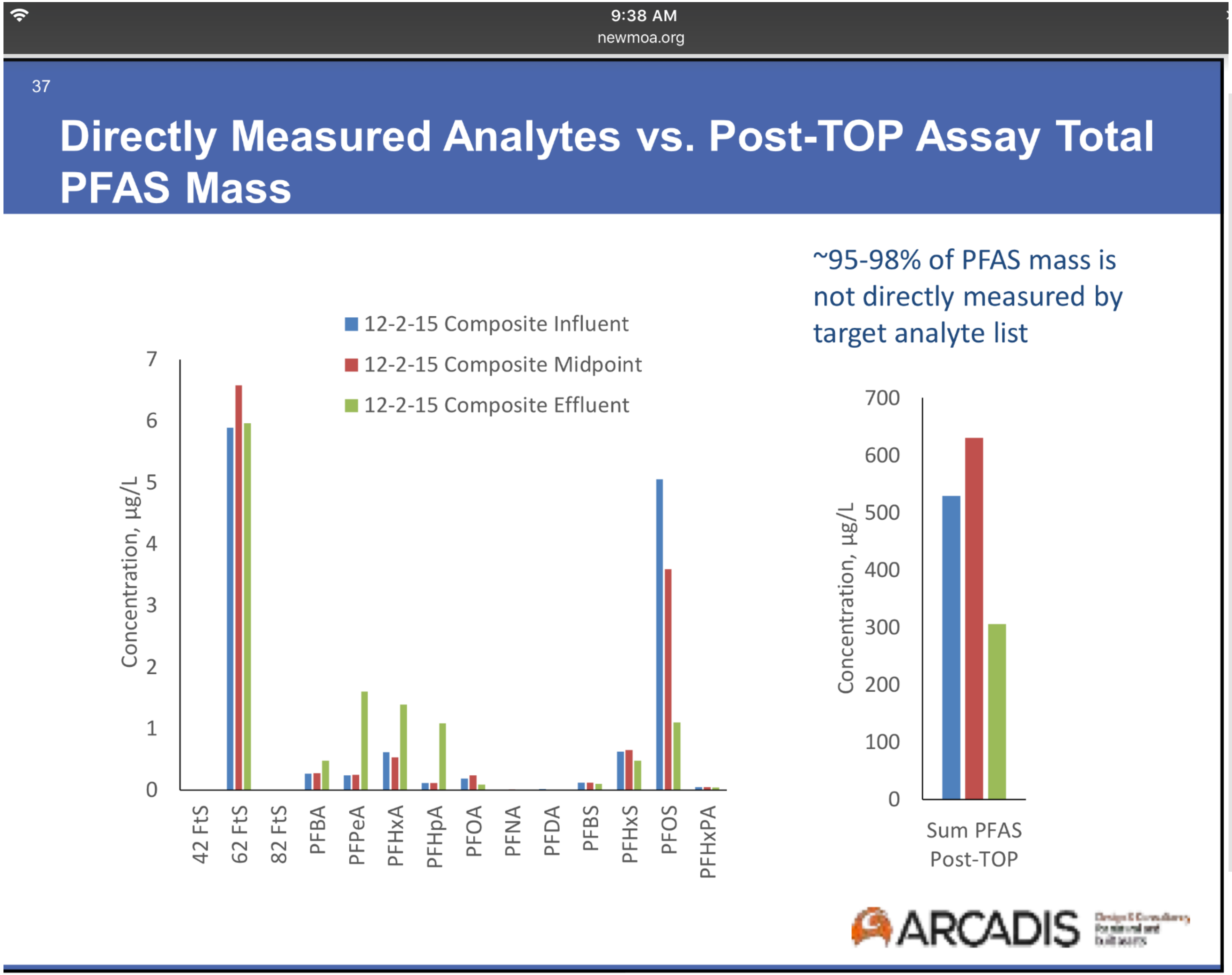
Testing: You only find what you look for.

Message: Look for everything you can find with existing methods.



	ng/L	ng/L
4:2 FtTAoS	990	210
6:2 FtTAoS	53,000	6,900
4:2 FtS	230	7,500
6:2 FtS	5,700	220,000
8:2 FtS	11,000	370
PFBS*	64,000	43,000
PFPeS	49,000	NA
PFHxS*	380,000	240,000
PFHpS	60,000	11,000
PFOS*	1,100,000	78,000
PFNS	3,000	NA
PFDS	<LOD	<LOD
PFBA	6,100	24,000
PFPeA	39,000	69,000
PFHxA*	27,000	130,000
PFHpA*	55,000	15,000
PFOA*	63,000	51,000
PFNA*	1,000	220
PFDA*	29[illegible]	<LOD

Most PFAS Mass is Missed with the Current Test Method.



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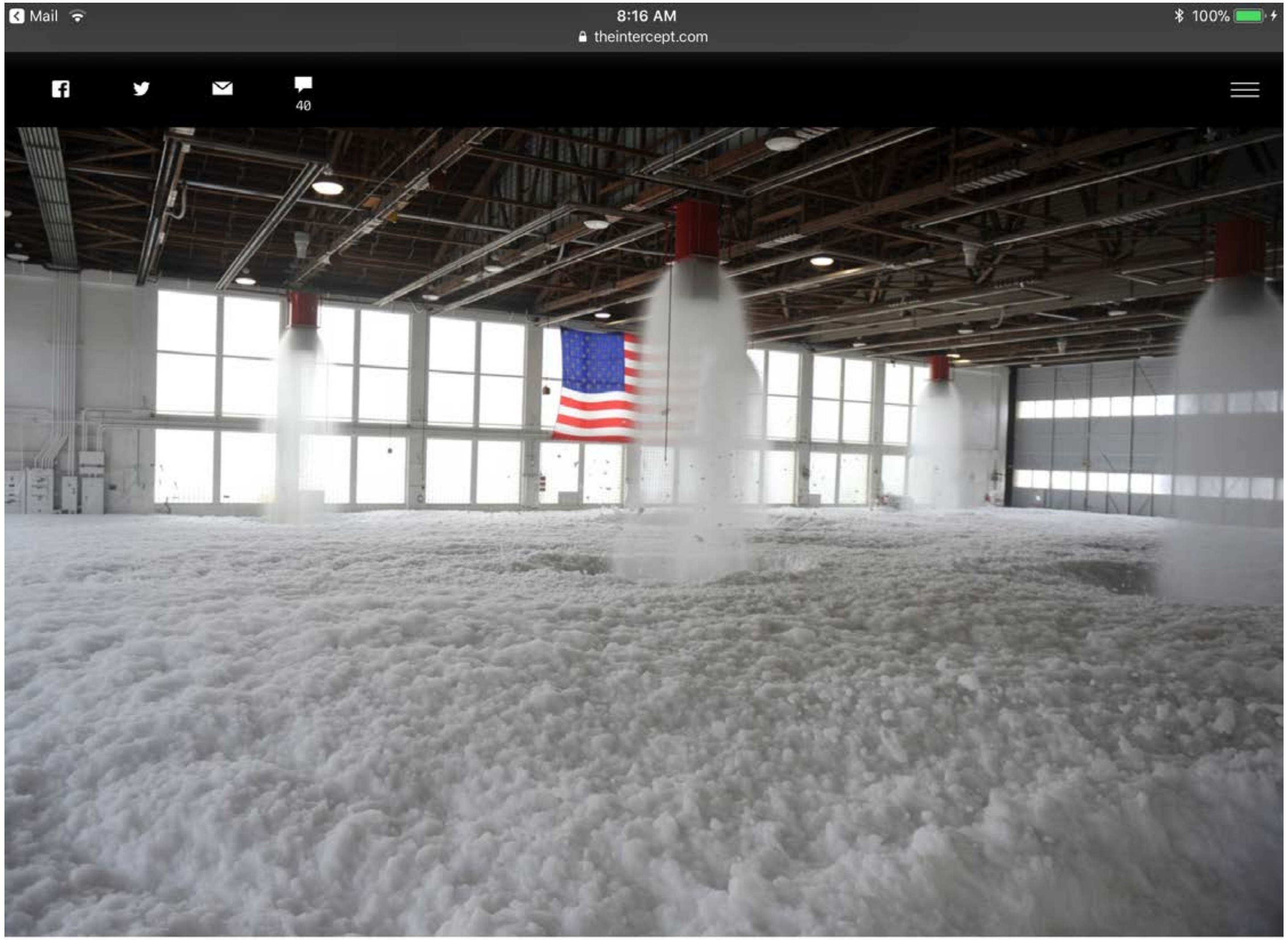
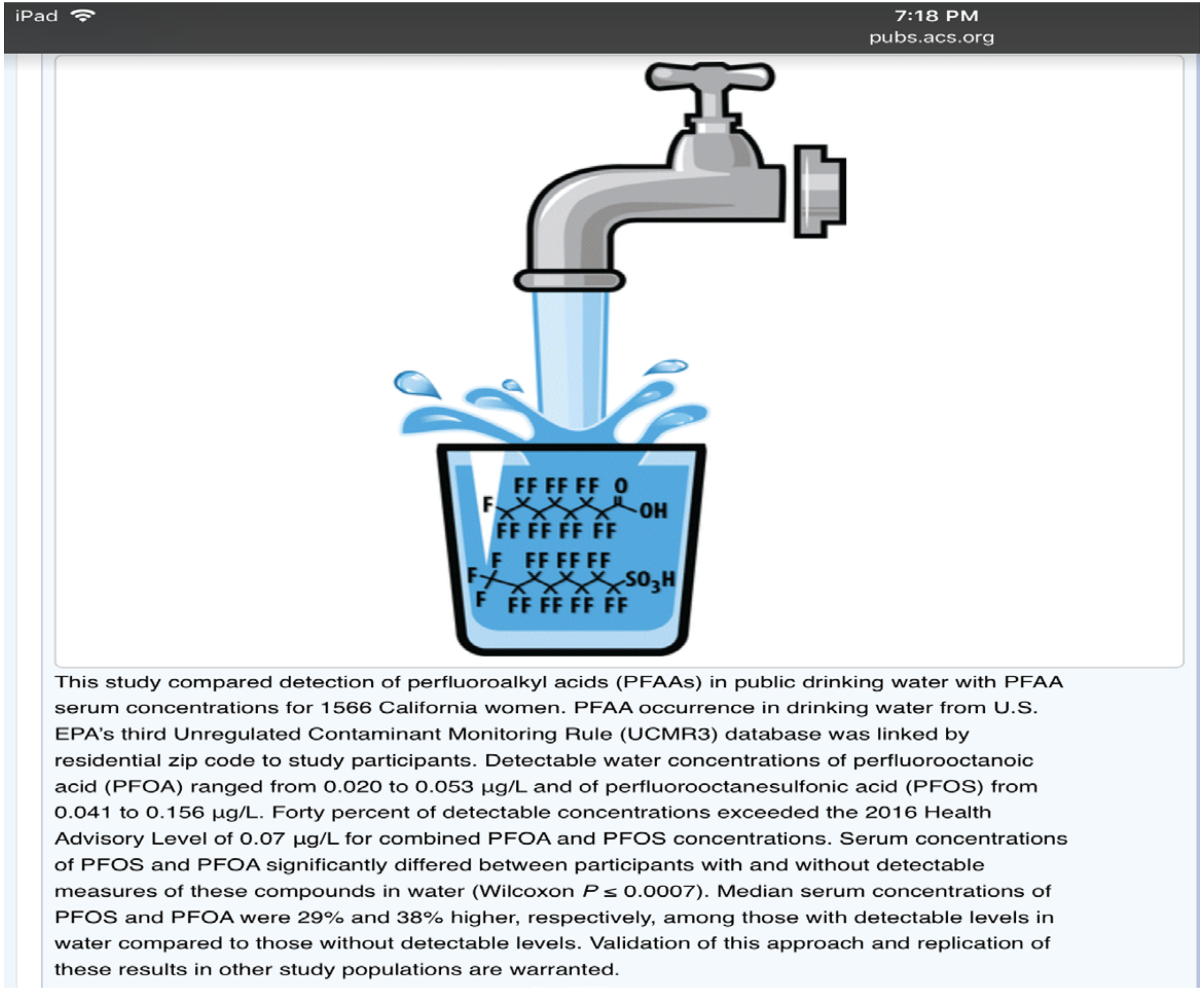
Directly Measured Analytes vs. Post-TOP Assay Total PFAS Mass

~95-98% of PFAS mass is not directly measured by target analyte list

AFFF ACCIDENTS HAPPEN



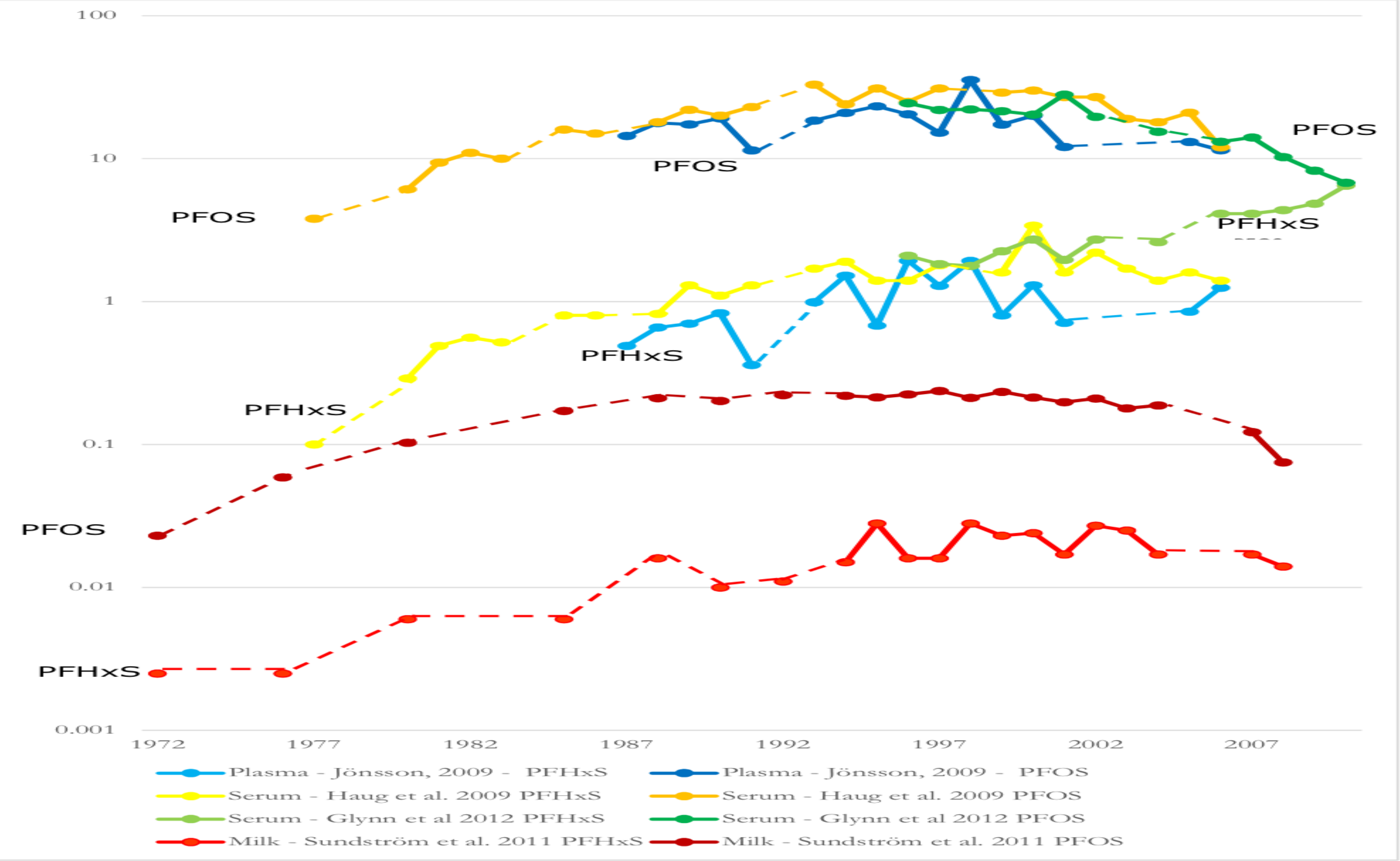
Drinking Water With PFAS Contamination Raises Your PFAS Body Burden by 29-38%.



This study compared detection of perfluoroalkyl acids (PFAAs) in public drinking water with PFAA serum concentrations for 1566 California women. PFAA occurrence in drinking water from U.S. EPA's third Unregulated Contaminant Monitoring Rule (UCMR3) database was linked by residential zip code to study participants. Detectable water concentrations of perfluorooctanoic acid (PFOA) ranged from 0.020 to 0.053 μg/L and of perfluorooctanesulfonic acid (PFOS) from 0.041 to 0.156 μg/L. Forty percent of detectable concentrations exceeded the 2016 Health Advisory Level of 0.07 μg/L for combined PFOA and PFOS concentrations. Serum concentrations of PFOS and PFOA significantly differed between participants with and without detectable measures of these compounds in water (Wilcoxon $P \leq 0.0007$). Median serum concentrations of PFOS and PFOA were 29% and 38% higher, respectively, among those with detectable levels in water compared to those without detectable levels. Validation of this approach and replication of these results in other study populations are warranted.

Plasma, Serum, and Breastmilk all have some PFAS Chemicals in them.

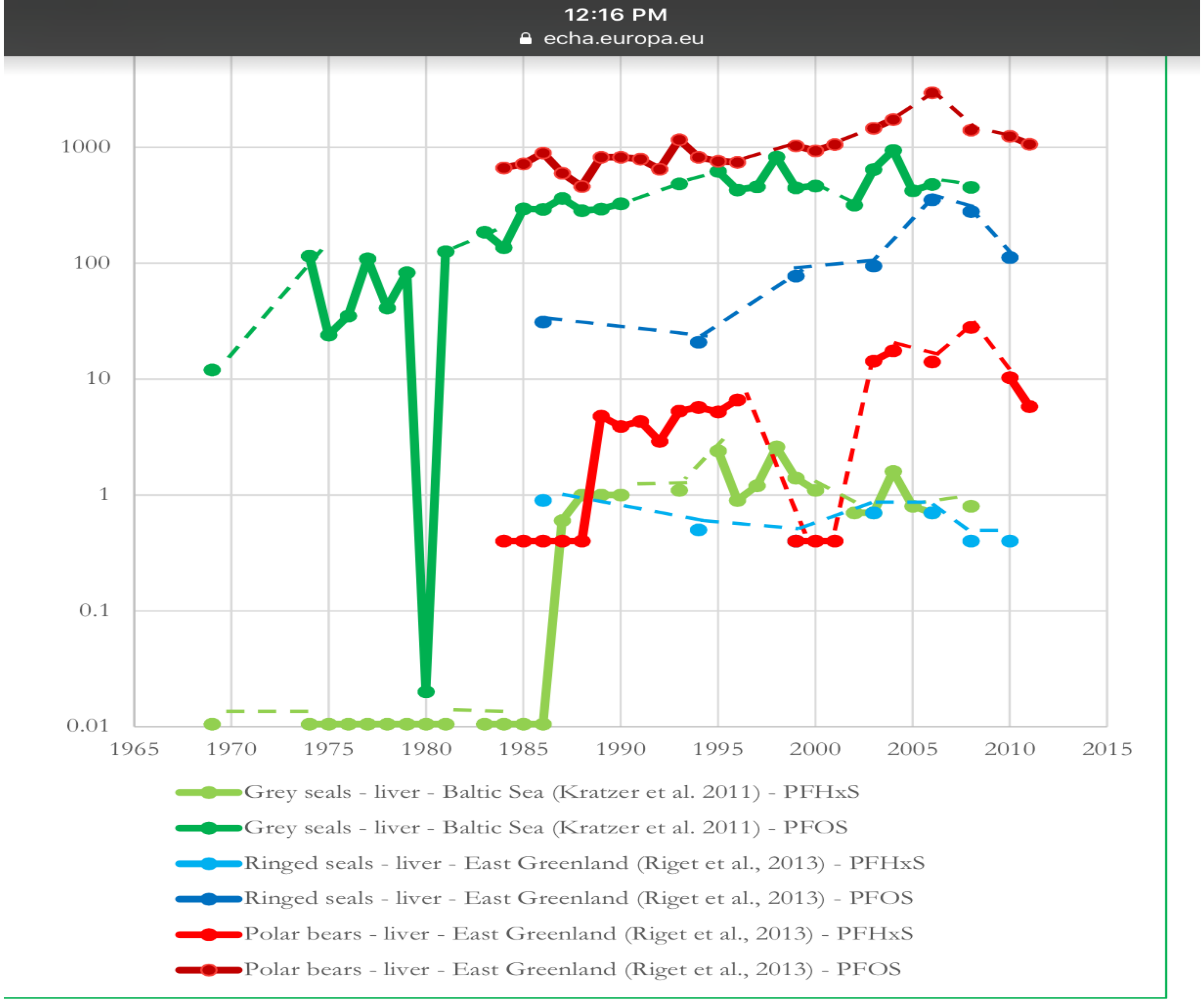
SVHC SUPPORT DOCUMENT - Perfluorohexane-1-sulphonic acid and its salts



8. Concentrations of PFHxS and PFOS in human plasma, serum and milk. Data from Haug *et*
9, Jönsson 2009, Sundström *et al.* 2011, and Glynn *et al.* 2012.

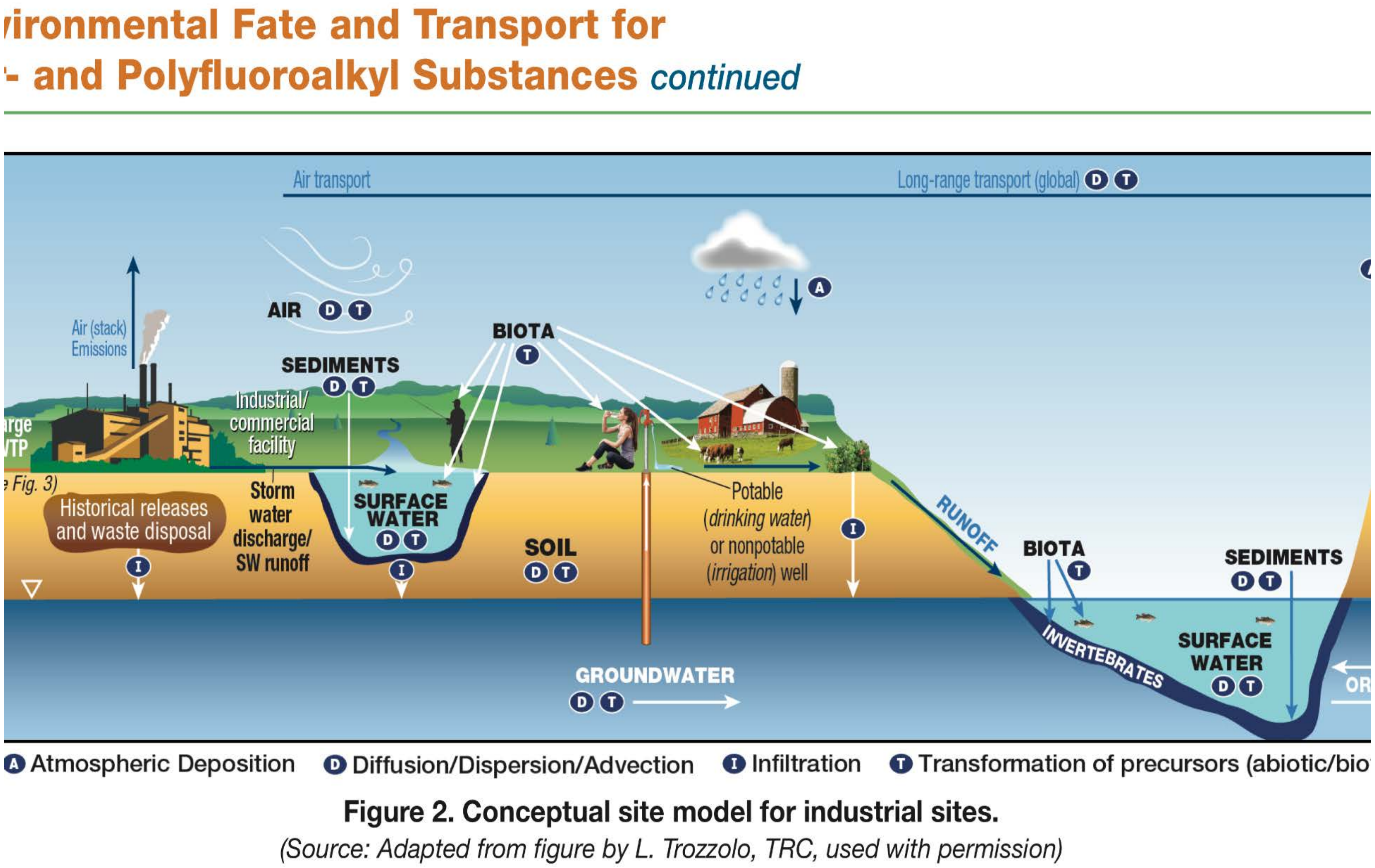
Polar Bears are Impacted: More PFAS in polar bears than PCBs, Dioxin, PBDEs, and Mercury Combined

PFHxS and PFOS In the Polar Bears and Seals of the Arctic



e 4. Concentrations of PFHxS and PFOS in seals and polar bears. Data from Kratzer *et*

How do PFAS Move Through the Environment?



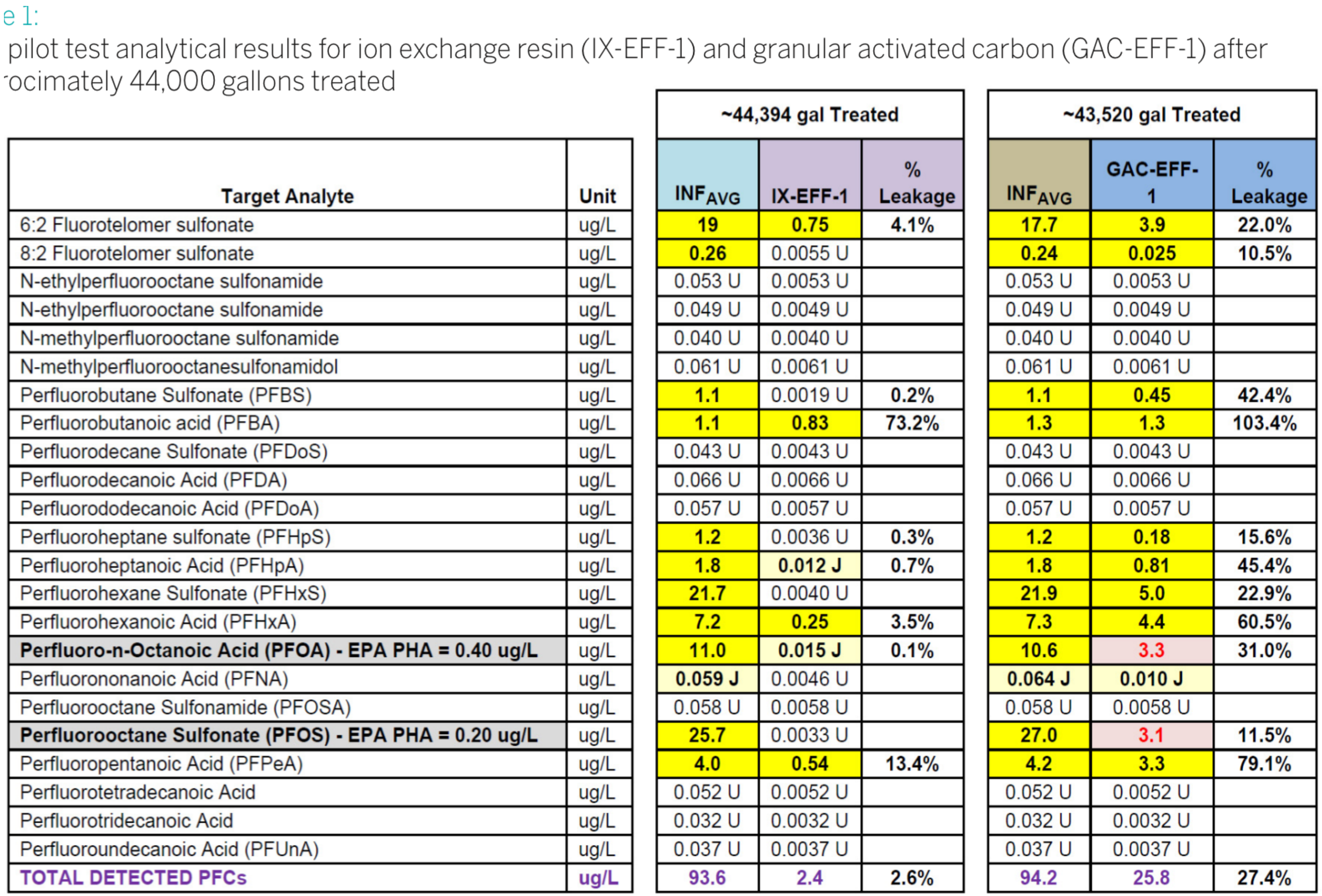
ironmental Fate and Transport for
- and Polyfluoroalkyl Substances *continued*

Ⓐ Atmospheric Deposition Ⓓ Diffusion/Dispersion/Advection Ⓘ Infiltration Ⓣ Transformation of precursors (abiotic/bio

Figure 2. Conceptual site model for industrial sites.

(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

Unfortunately “non-stick” chemicals breakthrough granular activated carbon.



e 1:
pilot test analytical results for ion exchange resin (IX-EFF-1) and granular activated carbon (GAC-EFF-1) after
ocimately 44,000 gallons treated

		~44,394 gal Treated			**~43,520 gal Treated**		
Target Analyte	**Unit**	**INF_{AVG}**	**IX-EFF-1**	**% Leakage**	**INF_{AVG}**	**GAC-EFF-1**	**% Leakage**
6:2 Fluorotelomer sulfonate	ug/L	**19**	**0.75**	**4.1%**	**17.7**	**3.9**	**22.0%**
8:2 Fluorotelomer sulfonate	ug/L	**0.26**	0.0055 U		**0.24**	**0.025**	**10.5%**
N-ethylperfluorooctane sulfonamide	ug/L	0.053 U	0.0053 U		0.053 U	0.0053 U	
N-ethylperfluorooctane sulfonamide	ug/L	0.049 U	0.0049 U		0.049 U	0.0049 U	
N-methylperfluorooctane sulfonamide	ug/L	0.040 U	0.0040 U		0.040 U	0.0040 U	
N-methylperfluorooctanesulfonamidol	ug/L	0.061 U	0.0061 U		0.061 U	0.0061 U	
Perfluorobutane Sulfonate (PFBS)	ug/L	**1.1**	0.0019 U	**0.2%**	**1.1**	**0.45**	**42.4%**
Perfluorobutanoic acid (PFBA)	ug/L	**1.1**	**0.83**	**73.2%**	**1.3**	**1.3**	**103.4%**
Perfluorodecane Sulfonate (PFDoS)	ug/L	0.043 U	0.0043 U		0.043 U	0.0043 U	
Perfluorodecanoic Acid (PFDA)	ug/L	0.066 U	0.0066 U		0.066 U	0.0066 U	
Perfluorododecanoic Acid (PFDoA)	ug/L	0.057 U	0.0057 U		0.057 U	0.0057 U	
Perfluoroheptane sulfonate (PFHpS)	ug/L	**1.2**	0.0036 U	**0.3%**	**1.2**	**0.18**	**15.6%**
Perfluoroheptanoic Acid (PFHpA)	ug/L	**1.8**	**0.012 J**	**0.7%**	**1.8**	**0.81**	**45.4%**
Perfluorohexane Sulfonate (PFHxS)	ug/L	**21.7**	0.0040 U		**21.9**	**5.0**	**22.9%**
Perfluorohexanoic Acid (PFHxA)	ug/L	**7.2**	**0.25**	**3.5%**	**7.3**	**4.4**	**60.5%**
Perfluoro-n-Octanoic Acid (PFOA) - EPA PHA = 0.40 ug/L	ug/L	**11.0**	**0.015 J**	**0.1%**	**10.6**	3.3	**31.0%**
Perfluorononanoic Acid (PFNA)	ug/L	**0.059 J**	0.0046 U		**0.064 J**	**0.010 J**	
Perfluorooctane Sulfonamide (PFOSA)	ug/L	0.058 U	0.0058 U		0.058 U	0.0058 U	
Perfluorooctane Sulfonate (PFOS) - EPA PHA = 0.20 ug/L	ug/L	**25.7**	0.0033 U		**27.0**	3.1	**11.5%**
Perfluoropentanoic Acid (PFPeA)	ug/L	**4.0**	**0.54**	**13.4%**	**4.2**	**3.3**	**79.1%**
Perfluorotetradecanoic Acid	ug/L	0.052 U	0.0052 U		0.052 U	0.0052 U	
Perfluorotridecanoic Acid	ug/L	0.032 U	0.0032 U		0.032 U	0.0032 U	
Perfluoroundecanoic Acid (PFUnA)	ug/L	0.037 U	0.0037 U		0.037 U	0.0037 U	
TOTAL DETECTED PFCs	**ug/L**	**93.6**	**2.4**	**2.6%**	**94.2**	**25.8**	**27.4%**

Complete PFAS Treatment technologies will be on the most expensive end of the scale.

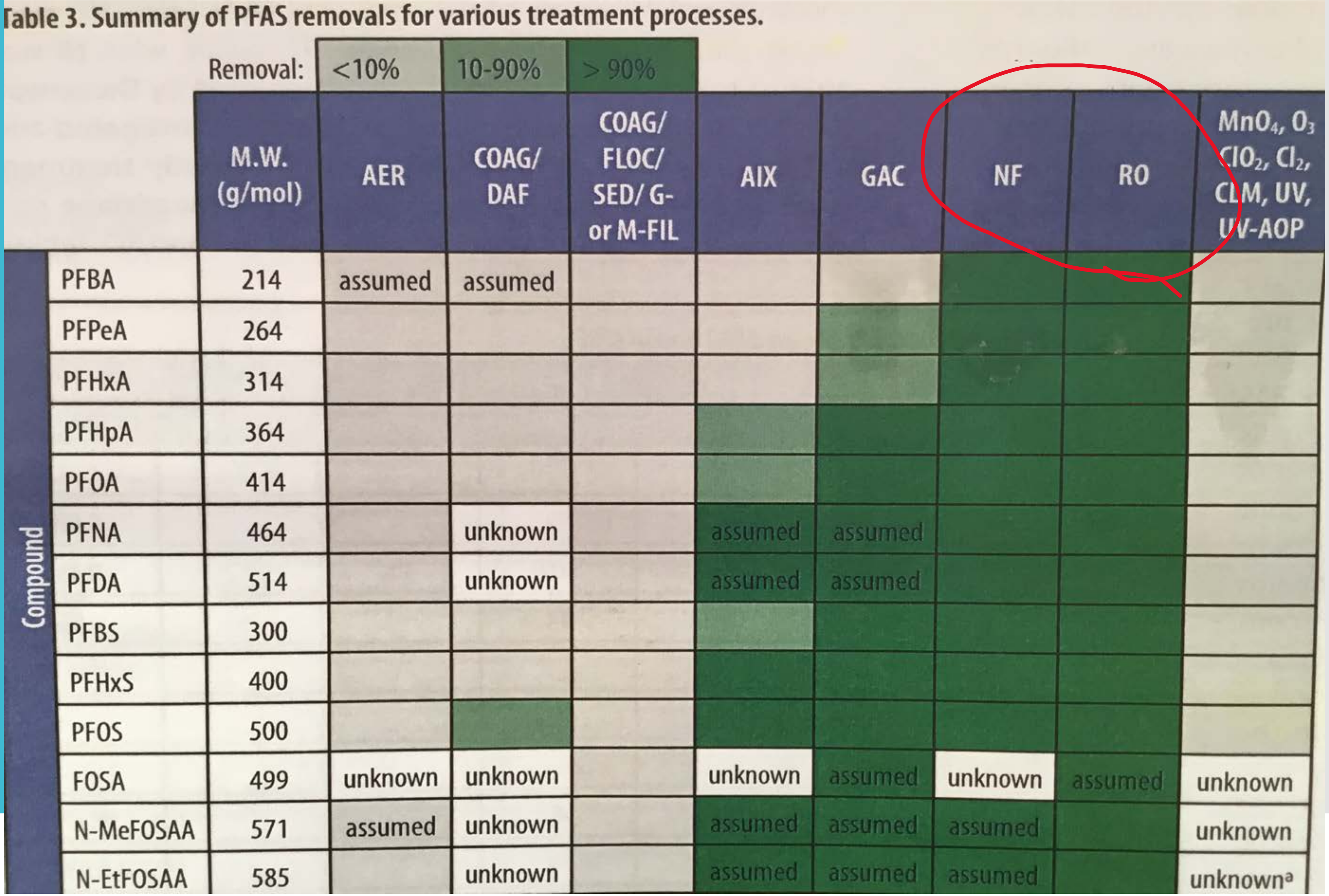
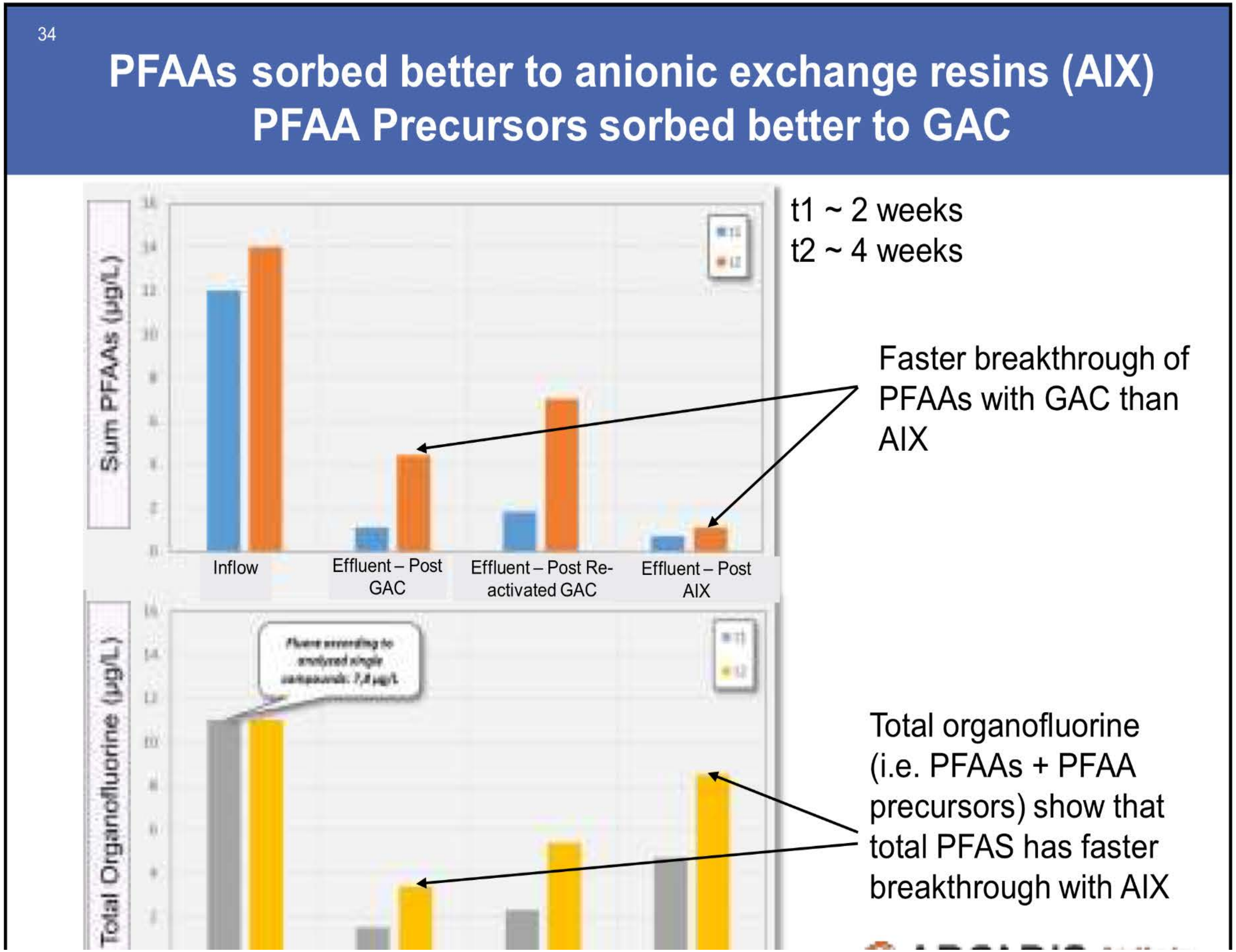


Table 3. Summary of PFAS removals for various treatment processes.

Removal: <10% | 10-90% | > 90%

Compound	M.W. (g/mol)	AER	COAG/ DAF	COAG/ FLOC/ SED/ G- or M-FIL	AIX	GAC	NF	RO	MnO$_4$, O$_3$ ClO$_2$, Cl$_2$, CLM, UV, UV-AOP
PFBA	214	<10% assumed	<10% assumed	<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%
PFOA	414	<10%	<10%	<10%	10-90%	> 90%	> 90%	> 90%	<10%
PFNA	464	<10%	unknown	<10%	> 90% assumed	> 90% assumed	> 90%	> 90%	<10%
PFDA	514	<10%	unknown	<10%	> 90% assumed	> 90% assumed	> 90%	> 90%	<10%
PFBS	300	<10%	<10%	<10%	10-90%	> 90%	> 90%	> 90%	<10%
PFHxS	400	<10%	<10%	<10%	> 90%	> 90%	> 90%	> 90%	<10%
PFOS	500	<10%	10-90%	<10%	> 90%	> 90%	> 90%	> 90%	<10%
FOSA	499	unknown	unknown	<10%	unknown	> 90% assumed	unknown	> 90% assumed	unknown
N-MeFOSAA	571	<10% assumed	unknown	<10%	> 90% assumed	> 90% assumed	> 90% assumed	> 90%	unknown
N-EtFOSAA	585	<10%	unknown	<10%	> 90% assumed	> 90% assumed	> 90% assumed	> 90%	unknown[a]

Unfortunately, Not all PFAS are Treated Effectively with the Same Treatment Systems.



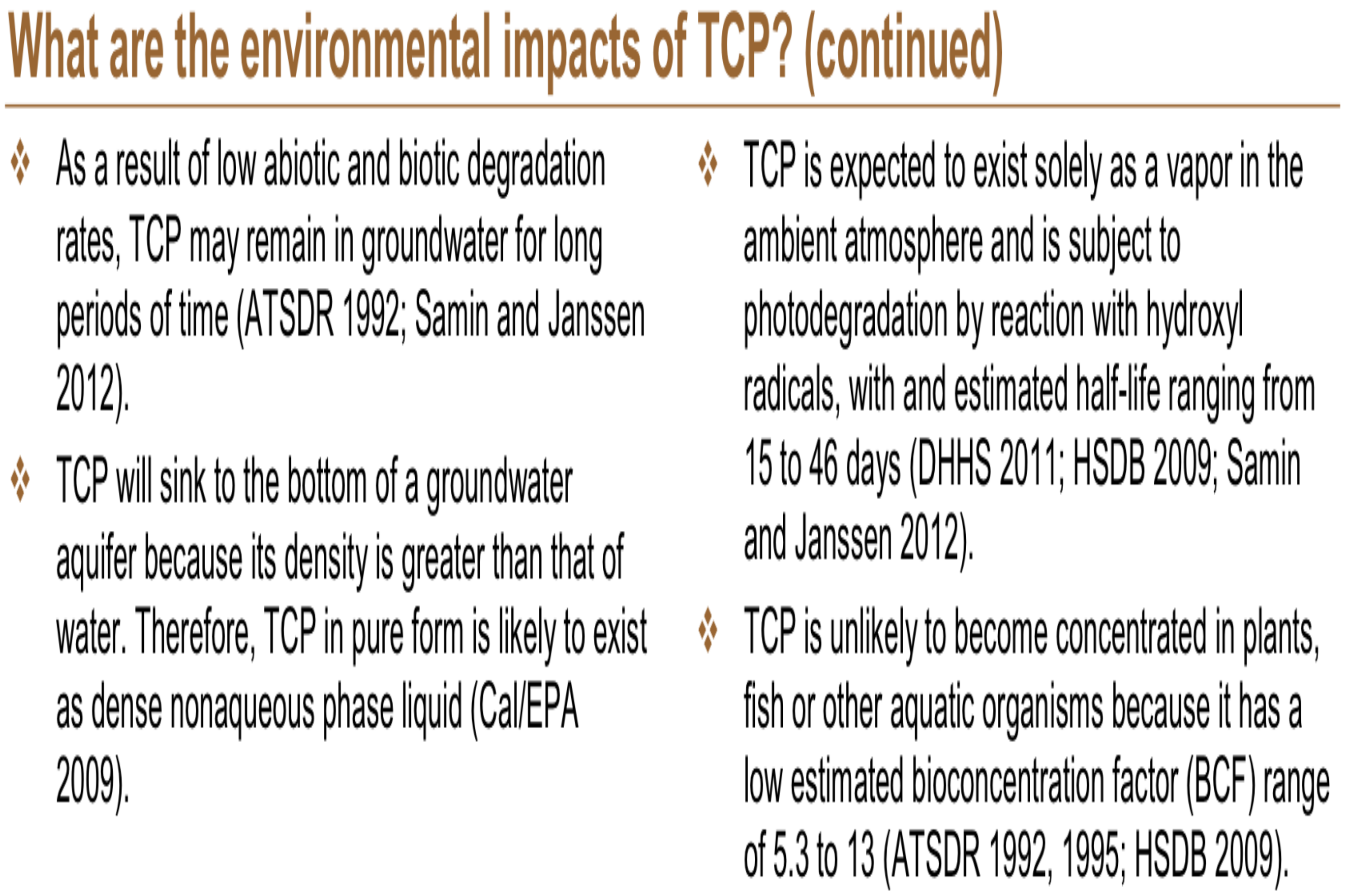
PFAAs sorbed better to anionic exchange resins (AIX)
PFAA Precursors sorbed better to GAC

t1 ~ 2 weeks
t2 ~ 4 weeks

Faster breakthrough of PFAAs with GAC than AIX

Total organofluorine (i.e. PFAAs + PFAA precursors) show that total PFAS has faster breakthrough with AIX

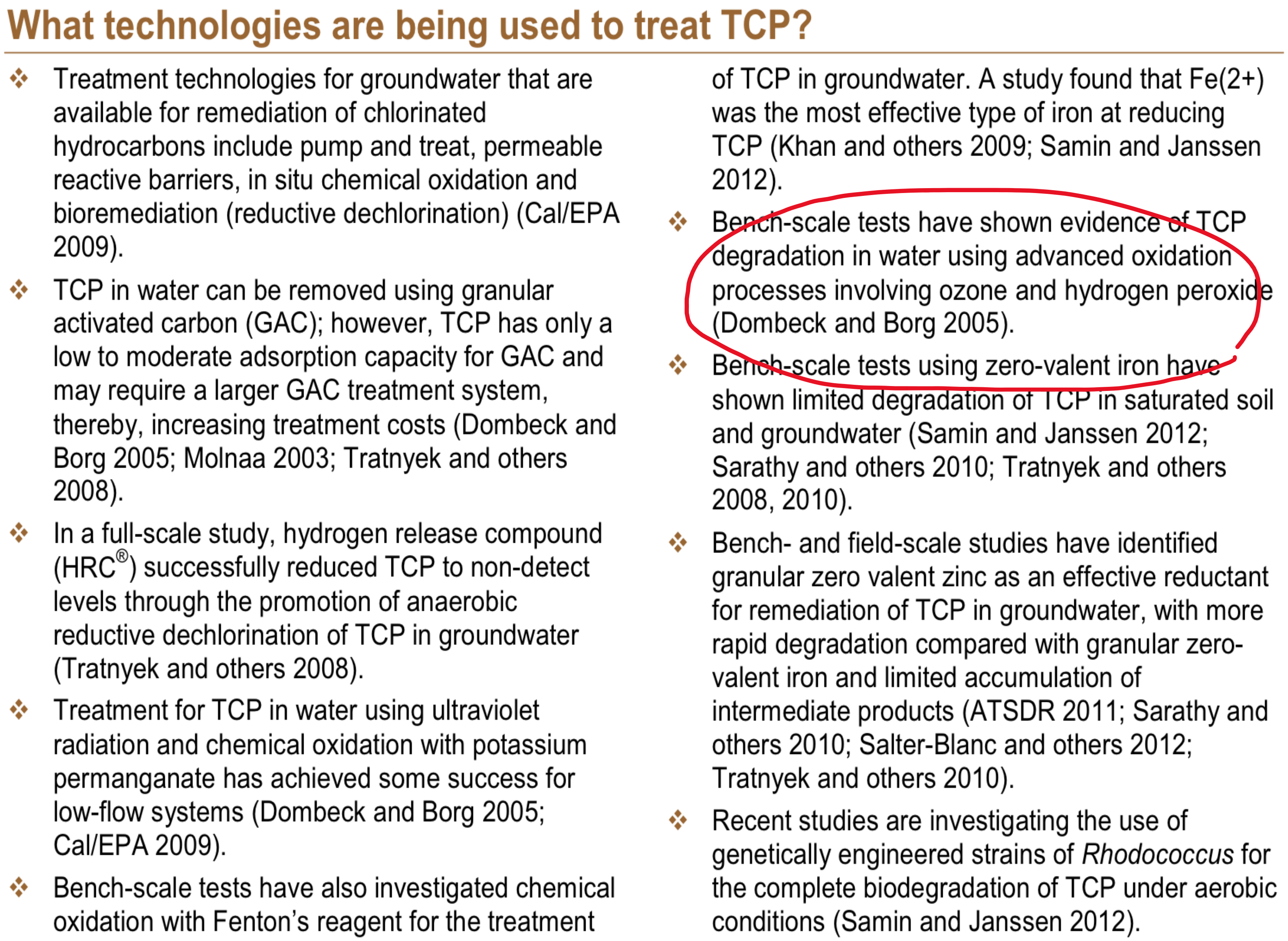
1,2,3 TCP



What are the environmental impacts of TCP? (continued)

- As a result of low abiotic and biotic degradation rates, TCP may remain in groundwater for long periods of time (ATSDR 1992; Samin and Janssen 2012).
- TCP will sink to the bottom of a groundwater aquifer because its density is greater than that of water. Therefore, TCP in pure form is likely to exist as dense nonaqueous phase liquid (Cal/EPA 2009).
- TCP is expected to exist solely as a vapor in the ambient atmosphere and is subject to photodegradation by reaction with hydroxyl radicals, with and estimated half-life ranging from 15 to 46 days (DHHS 2011; HSDB 2009; Samin and Janssen 2012).
- TCP is unlikely to become concentrated in plants, fish or other aquatic organisms because it has a low estimated bioconcentration factor (BCF) range of 5.3 to 13 (ATSDR 1992, 1995; HSDB 2009).

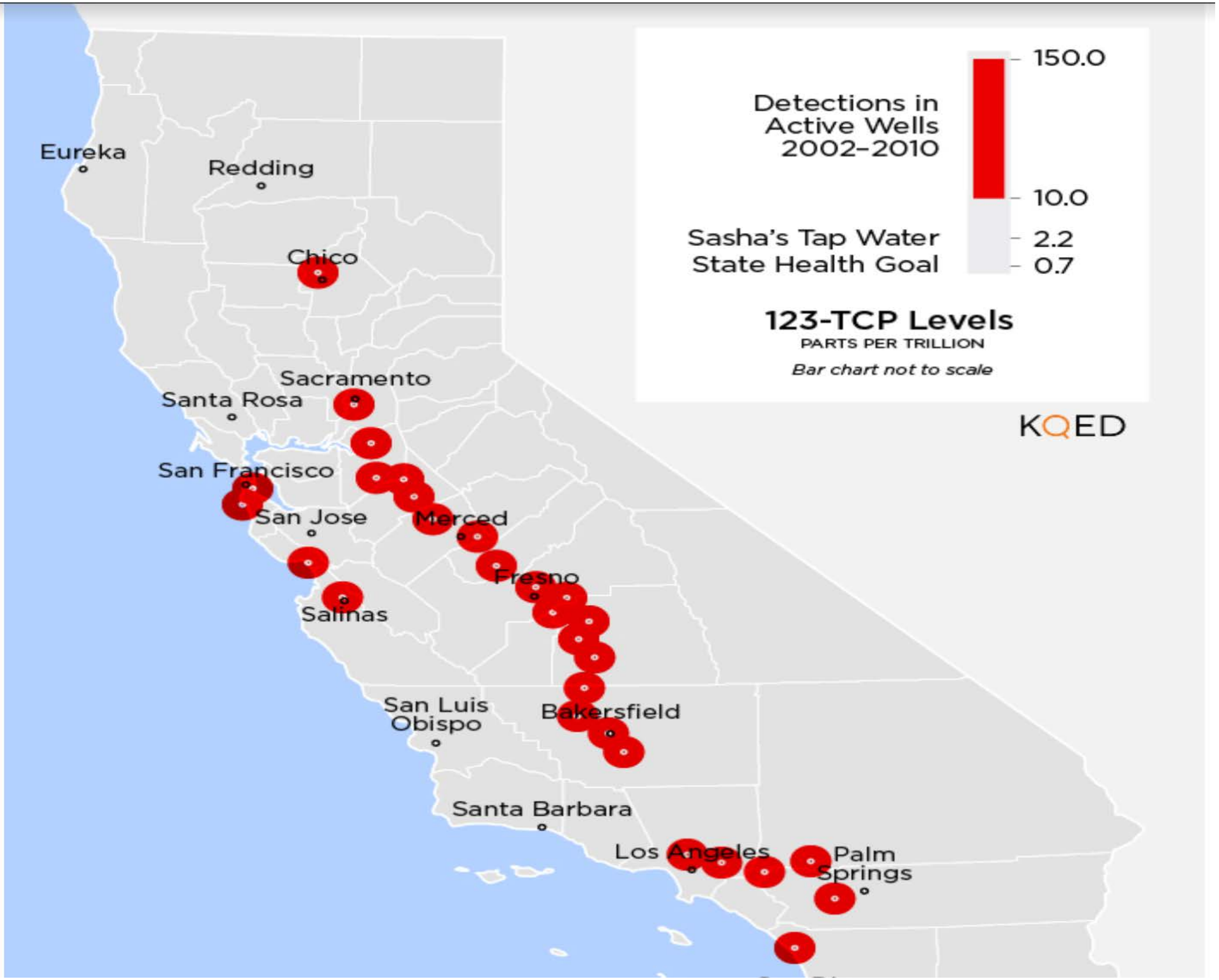
1,2,3 TCP Treatment Technologies



What technologies are being used to treat TCP?

- Treatment technologies for groundwater that are available for remediation of chlorinated hydrocarbons include pump and treat, permeable reactive barriers, in situ chemical oxidation and bioremediation (reductive dechlorination) (Cal/EPA 2009).
- TCP in water can be removed using granular activated carbon (GAC); however, TCP has only a low to moderate adsorption capacity for GAC and may require a larger GAC treatment system, thereby, increasing treatment costs (Dombeck and Borg 2005; Molnaa 2003; Tratnyek and others 2008).
- In a full-scale study, hydrogen release compound (HRC®) successfully reduced TCP to non-detect levels through the promotion of anaerobic reductive dechlorination of TCP in groundwater (Tratnyek and others 2008).
- Treatment for TCP in water using ultraviolet radiation and chemical oxidation with potassium permanganate has achieved some success for low-flow systems (Dombeck and Borg 2005; Cal/EPA 2009).
- Bench-scale tests have also investigated chemical oxidation with Fenton's reagent for the treatment of TCP in groundwater. A study found that Fe(2+) was the most effective type of iron at reducing TCP (Khan and others 2009; Samin and Janssen 2012).
- Bench-scale tests have shown evidence of TCP degradation in water using advanced oxidation processes involving ozone and hydrogen peroxide (Dombeck and Borg 2005).
- Bench-scale tests using zero-valent iron have shown limited degradation of TCP in saturated soil and groundwater (Samin and Janssen 2012; Sarathy and others 2010; Tratnyek and others 2008, 2010).
- Bench- and field-scale studies have identified granular zero valent zinc as an effective reductant for remediation of TCP in groundwater, with more rapid degradation compared with granular zero-valent iron and limited accumulation of intermediate products (ATSDR 2011; Sarathy and others 2010; Salter-Blanc and others 2012; Tratnyek and others 2010).
- Recent studies are investigating the use of genetically engineered strains of *Rhodococcus* for the complete biodegradation of TCP under aerobic conditions (Samin and Janssen 2012).

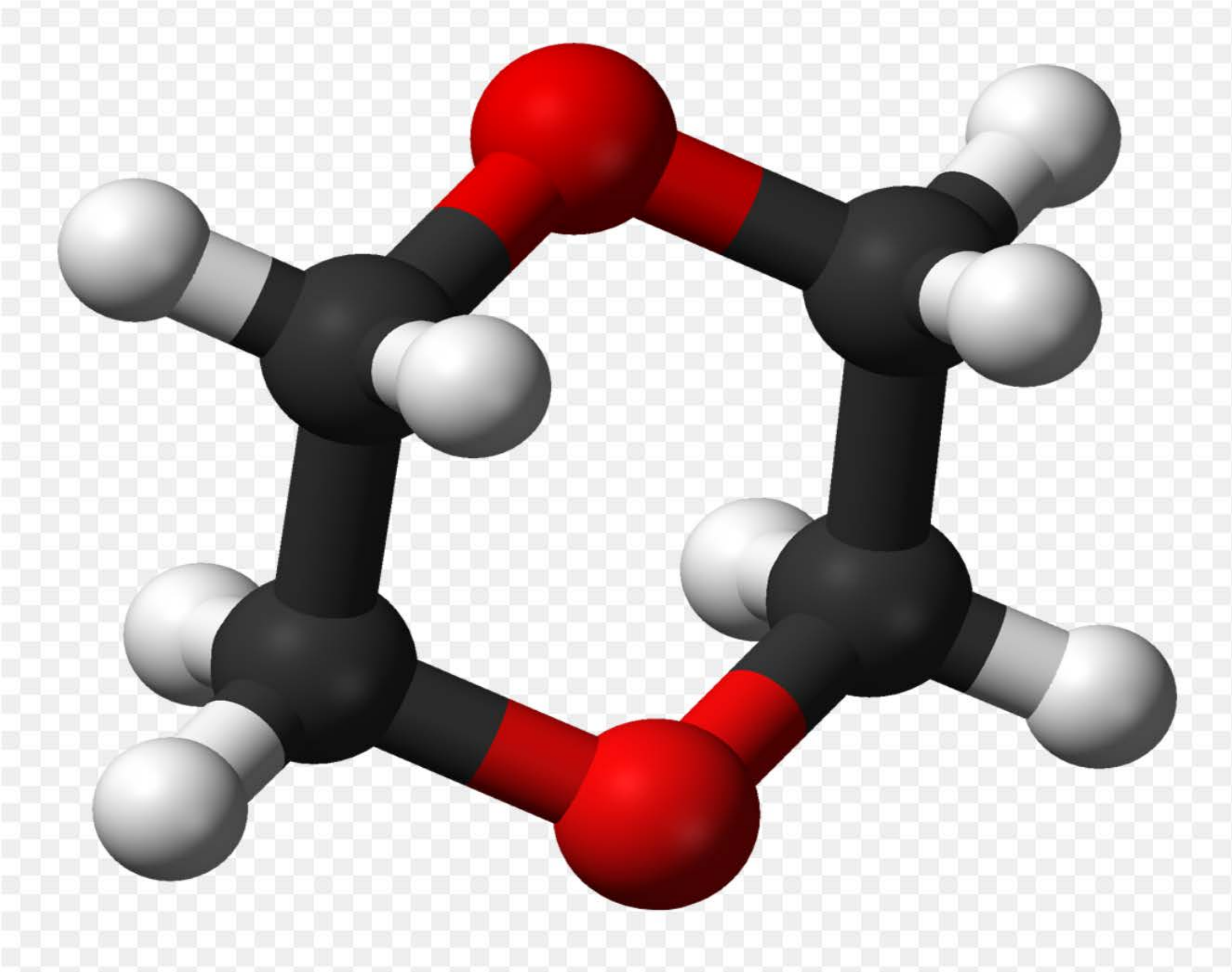
What is the Incidence of 1,2,3 TCP in California?



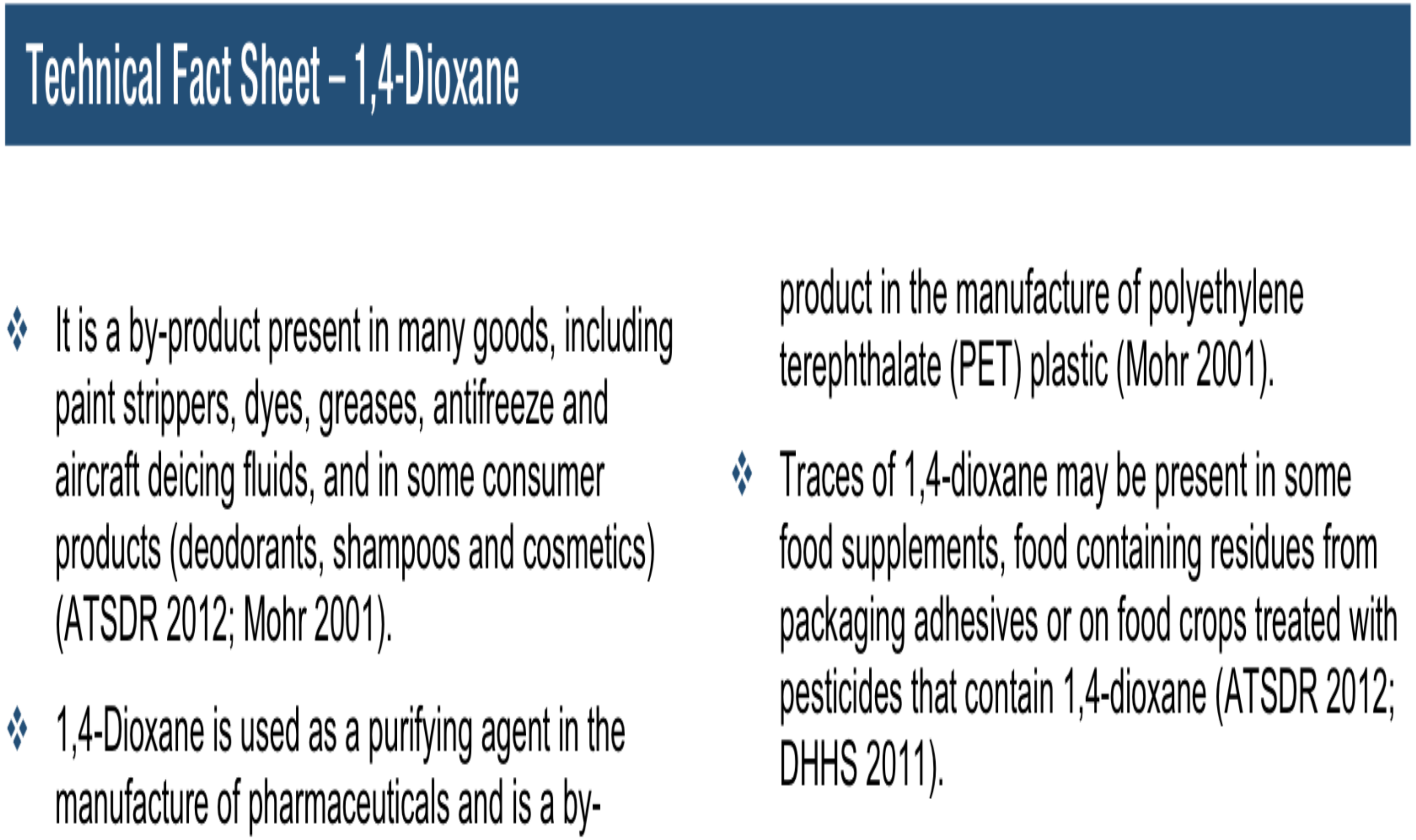
To sum up on 1,2,3 TCP:

- Very expensive to remove from drinking water.
- Those Environmental Justice communities least able to absorb the costs are going to bear the burden of cleanup.
- The state needs a plan on how to help those Communities.

1,4 Dioxane



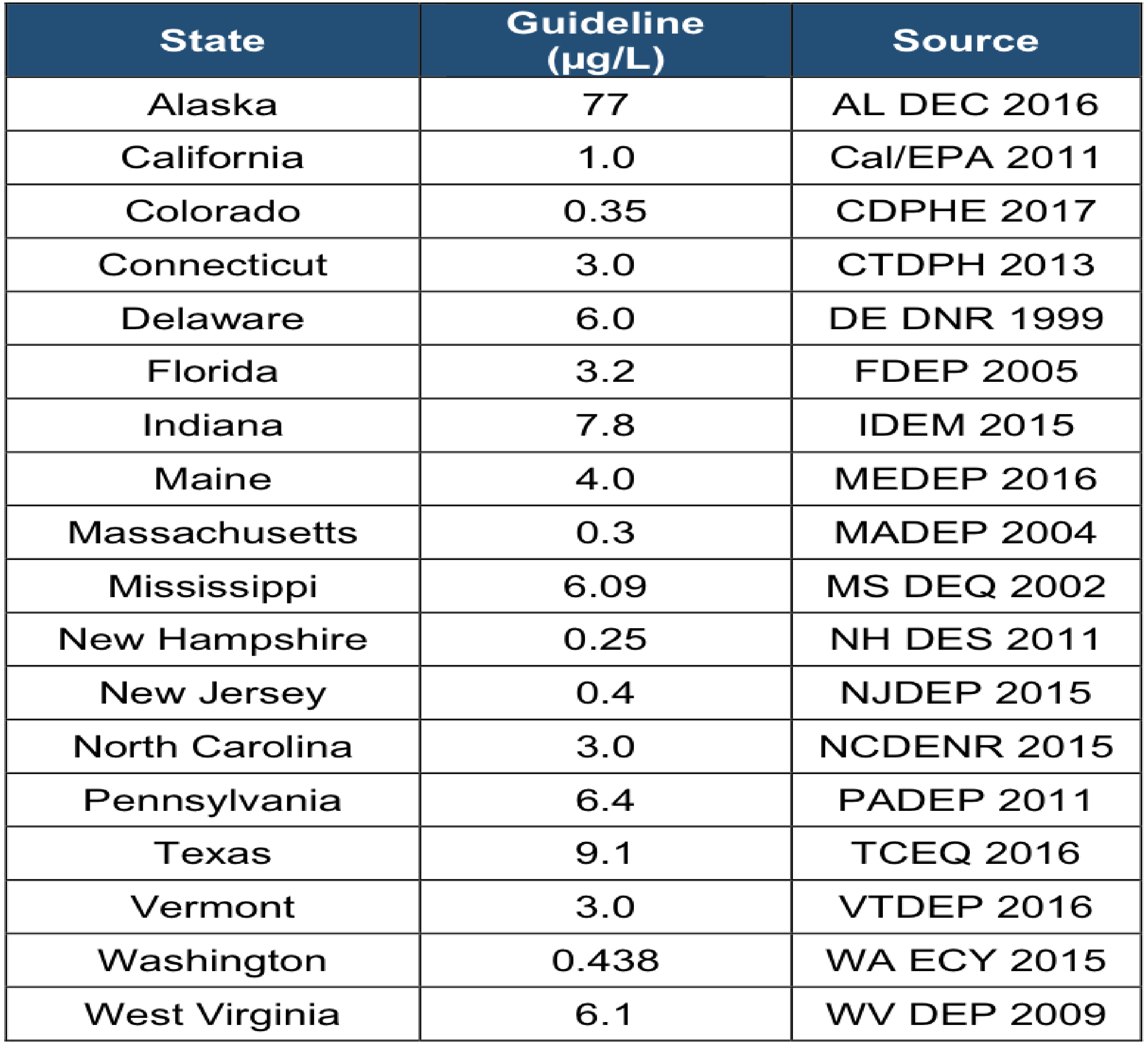
1,4 Dioxane: What is it used for?



Technical Fact Sheet – 1,4-Dioxane

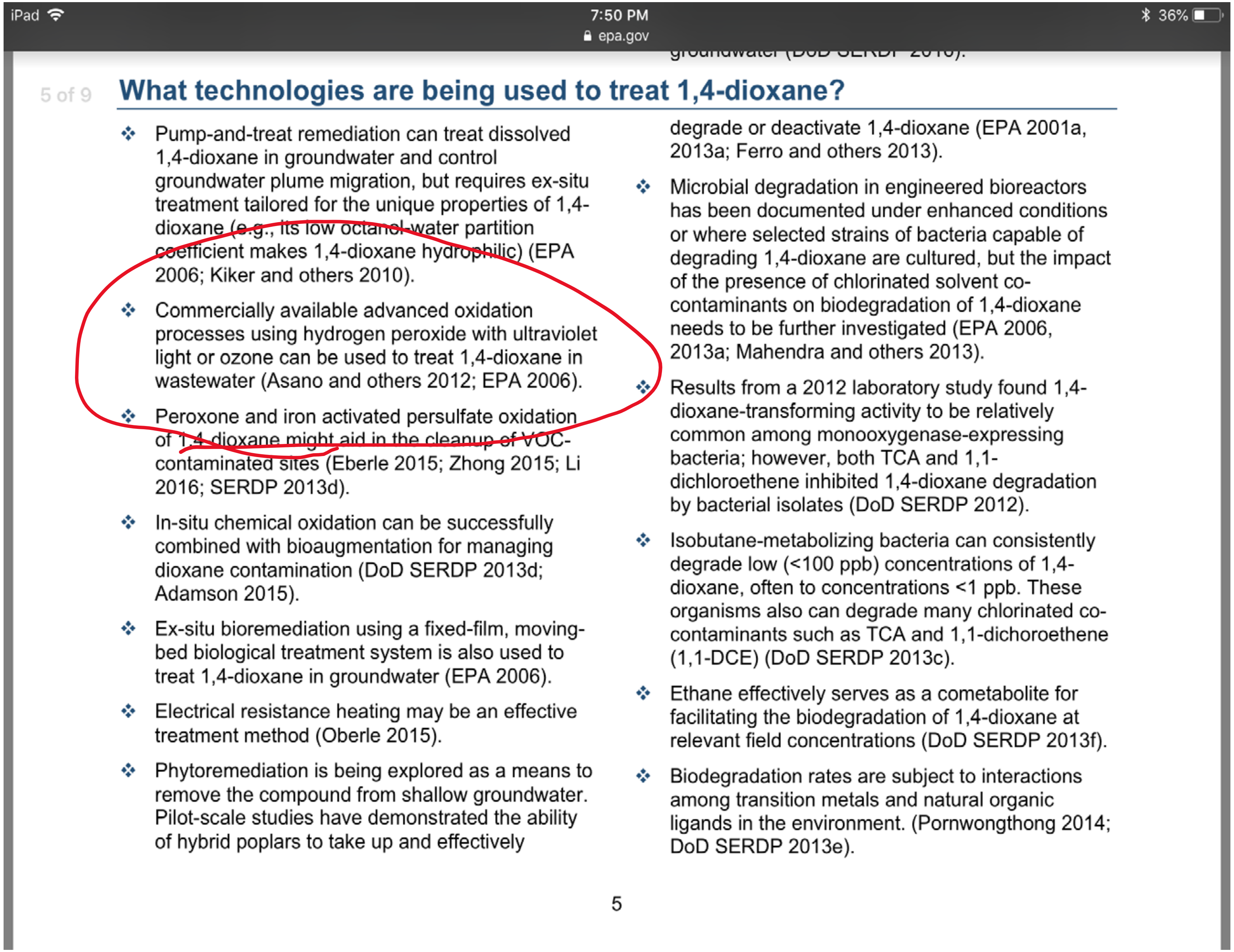
- It is a by-product present in many goods, including paint strippers, dyes, greases, antifreeze and aircraft deicing fluids, and in some consumer products (deodorants, shampoos and cosmetics) (ATSDR 2012; Mohr 2001).
- 1,4-Dioxane is used as a purifying agent in the manufacture of pharmaceuticals and is a by-product in the manufacture of polyethylene terephthalate (PET) plastic (Mohr 2001).
- Traces of 1,4-dioxane may be present in some food supplements, food containing residues from packaging adhesives or on food crops treated with pesticides that contain 1,4-dioxane (ATSDR 2012; DHHS 2011).

1,4 Dioxane: Commonly found with solvent plumes, very toxic.



State	Guideline (µg/L)	Source
Alaska	77	AL DEC 2016
California	1.0	Cal/EPA 2011
Colorado	0.35	CDPHE 2017
Connecticut	3.0	CTDPH 2013
Delaware	6.0	DE DNR 1999
Florida	3.2	FDEP 2005
Indiana	7.8	IDEM 2015
Maine	4.0	MEDEP 2016
Massachusetts	0.3	MADEP 2004
Mississippi	6.09	MS DEQ 2002
New Hampshire	0.25	NH DES 2011
New Jersey	0.4	NJDEP 2015
North Carolina	3.0	NCDENR 2015
Pennsylvania	6.4	PADEP 2011
Texas	9.1	TCEQ 2016
Vermont	3.0	VTDEP 2016
Washington	0.438	WA ECY 2015
West Virginia	6.1	WV DEP 2009

1,4 Dioxane: Treatment Technologies



groundwater (DoD SERDP 2016).

What technologies are being used to treat 1,4-dioxane?

- Pump-and-treat remediation can treat dissolved 1,4-dioxane in groundwater and control groundwater plume migration, but requires ex-situ treatment tailored for the unique properties of 1,4-dioxane (e.g., its low octanol-water partition coefficient makes 1,4-dioxane hydrophilic) (EPA 2006; Kiker and others 2010).
- Commercially available advanced oxidation processes using hydrogen peroxide with ultraviolet light or ozone can be used to treat 1,4-dioxane in wastewater (Asano and others 2012; EPA 2006).
- Peroxone and iron activated persulfate oxidation of 1,4-dioxane might aid in the cleanup of VOC-contaminated sites (Eberle 2015; Zhong 2015; Li 2016; SERDP 2013d).
- In-situ chemical oxidation can be successfully combined with bioaugmentation for managing dioxane contamination (DoD SERDP 2013d; Adamson 2015).
- Ex-situ bioremediation using a fixed-film, moving-bed biological treatment system is also used to treat 1,4-dioxane in groundwater (EPA 2006).
- Electrical resistance heating may be an effective treatment method (Oberle 2015).
- Phytoremediation is being explored as a means to remove the compound from shallow groundwater. Pilot-scale studies have demonstrated the ability of hybrid poplars to take up and effectively degrade or deactivate 1,4-dioxane (EPA 2001a, 2013a; Ferro and others 2013).
- Microbial degradation in engineered bioreactors has been documented under enhanced conditions or where selected strains of bacteria capable of degrading 1,4-dioxane are cultured, but the impact of the presence of chlorinated solvent co-contaminants on biodegradation of 1,4-dioxane needs to be further investigated (EPA 2006, 2013a; Mahendra and others 2013).
- Results from a 2012 laboratory study found 1,4-dioxane-transforming activity to be relatively common among monooxygenase-expressing bacteria; however, both TCA and 1,1-dichloroethene inhibited 1,4-dioxane degradation by bacterial isolates (DoD SERDP 2012).
- Isobutane-metabolizing bacteria can consistently degrade low (<100 ppb) concentrations of 1,4-dioxane, often to concentrations <1 ppb. These organisms also can degrade many chlorinated co-contaminants such as TCA and 1,1-dichoroethene (1,1-DCE) (DoD SERDP 2013c).
- Ethane effectively serves as a cometabolite for facilitating the biodegradation of 1,4-dioxane at relevant field concentrations (DoD SERDP 2013f).
- Biodegradation rates are subject to interactions among transition metals and natural organic ligands in the environment. (Pornwongthong 2014; DoD SERDP 2013e).

1,4 Dioxane: Second Verse same as The First.

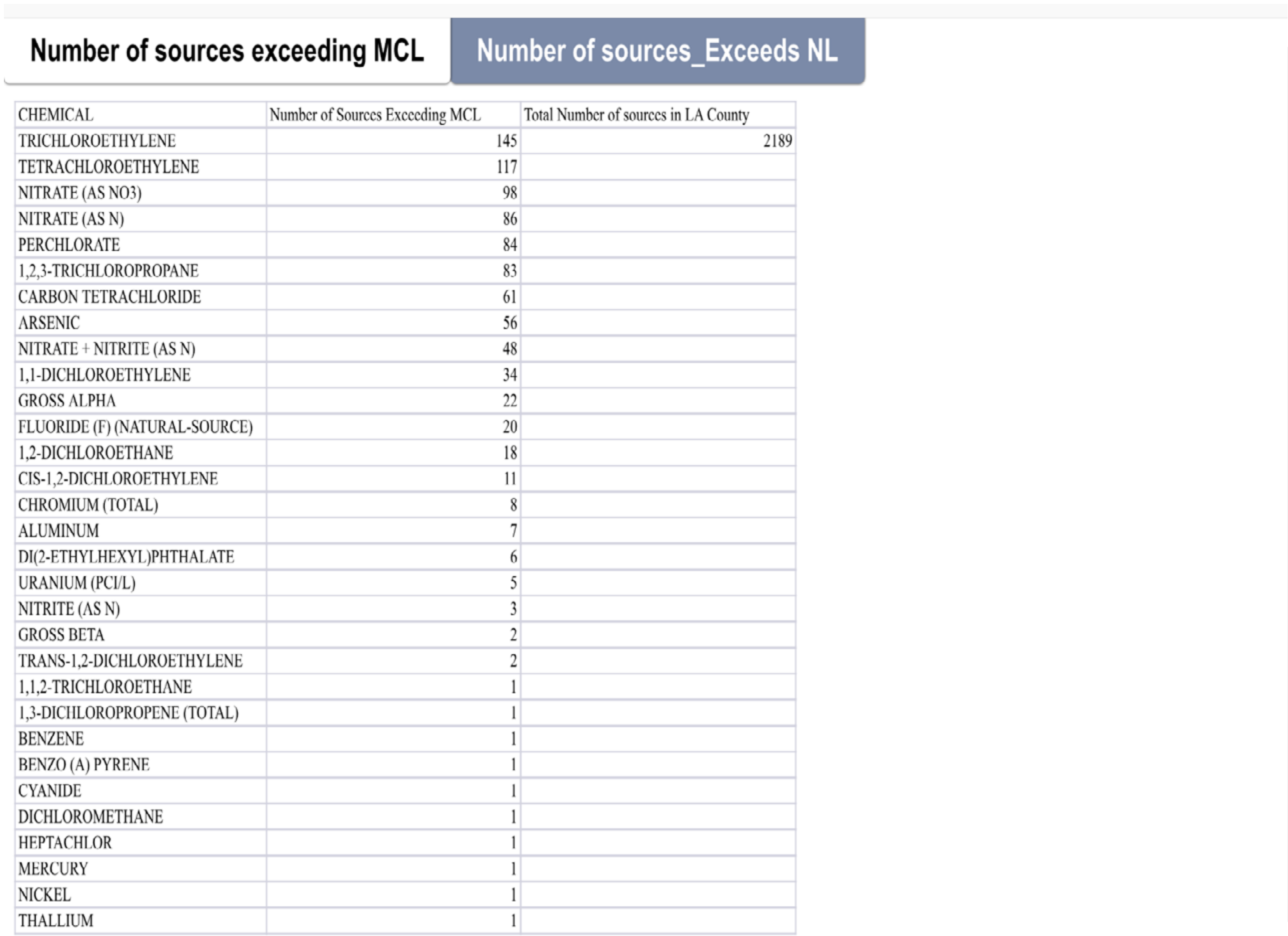
- Communities impacted by some of the other contaminant plumes will also find 1,4 Dioxane in their water.
- It will need a different treatment technology.
- It will be expensive.
- Those communities least able to afford the cost will be the most impacted.
- Sound familiar?

Groundwater Contamination:

The Never-Ending Story

- We knew in the 1960s that there were chemicals that were getting into groundwater. This was the impetus for the Resource Conservation and Recovery Act.
- We still do not have any program for the pre-market review of the over 85,000 Chemicals in commercial production.

So… What's the damages?



CHEMICAL	Number of Sources Exceeding MCL	Total Number of sources in LA County
TRICHLOROETHYLENE	145	2189
TETRACHLOROETHYLENE	117	
NITRATE (AS NO3)	98	
NITRATE (AS N)	86	
PERCHLORATE	84	
1,2,3-TRICHLOROPROPANE	83	
CARBON TETRACHLORIDE	61	
ARSENIC	56	
NITRATE + NITRITE (AS N)	48	
1,1-DICHLOROETHYLENE	34	
GROSS ALPHA	22	
FLUORIDE (F) (NATURAL-SOURCE)	20	
1,2-DICHLOROETHANE	18	
CIS-1,2-DICHLOROETHYLENE	11	
CHROMIUM (TOTAL)	8	
ALUMINUM	7	
DI(2-ETHYLHEXYL)PHTHALATE	6	
URANIUM (PCI/L)	5	
NITRITE (AS N)	3	
GROSS BETA	2	
TRANS-1,2-DICHLOROETHYLENE	2	
1,1,2-TRICHLOROETHANE	1	
1,3-DICHLOROPROPENE (TOTAL)	1	
BENZENE	1	
BENZO (A) PYRENE	1	
CYANIDE	1	
DICHLOROMETHANE	1	
HEPTACHLOR	1	
MERCURY	1	
NICKEL	1	
THALLIUM	1	

Take Away Message

- We need a better plan on Groundwater!
- We need a comprehensive strategy that includes keeping contaminants out of our water resources.