Workshop on PFAS Chemicals-State Water Resources Control Board:

March 6, 2019

Jane Williams

- Executive Director
- California Communities Against Toxics
- •PFAS Chemicals: An Emerging Threat to Groundwater

\$EPA

Sources of PFAS in the Environment

Many Threats to Groundwater from PFAS Uses.



- 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

Global Problems: PFAS Contamination is now one of them.



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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.

Conceptual Site Model of a Fire Training Area



Increasing mobility of shorter perfluoroalkyl chain PFAS



Groundwater Sampling

This is a huge Contamination Problem for the DOD.

Component	Total Installations with known or suspected release of PFOS/PFOA (as of August 31, 2017)	Number of Installations Sampled where results exceeded EPA LHA (as of August 31, 2017)	Total number of groundwater wells sampled	Number of groundwater wells that tested above the EPA LHA
Army	64	9	258	104
Navy/USMC	127	40	1,368	784
Air Force	203	39	1,022	719
DLA	7	2	20	14
Total	401	90	2,668	1,621

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< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></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*	2 ° 18 of 25	<lod< td=""></lod<>

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

Most PFAS Mass is Missed with the Current Test Method. 37



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





There is a Research Agenda for PFAS by DOD/DOE



This figure illustrates the Statements of Need that have been released under the SERDP since 2011, as well as the ESTCP projects that have been initiated since 2015. The SERDP Statements of Need are specific topics released as part of the annual solicitation that describe the research areas of interest for that fiscal year. Click on a Statement of Need to view a summary of the research areas of as well as a list of the project selected under that Statement of Need. Within these summaries, each project title links to a full description of the project, as well as any SERDP reports that have been published as part of the project. Each ESTCP topic listed represents a single topic; click the project title to go to the project web page.

The hoves along the top of the graph illustrate workshops that have been held to develop a strategic plan for addressing issues associated with DEASS. A summary report was prepared for each

AFFF ACCIDENTS HAPPEN



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Common Consumer Products Contain PFAS Chemicals

Perfluorooctane sulphonate (PFOS) Kemi.se , se , substance-groups , perflu...

May 17, 2017 · PFOS has been used in the past in cleaning products, in fire fighting foams and as an ... attention has been drawn to PFOS in connection with a major manufacturer, 3M, having decided to phase out its ...



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

iPad 🗢



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 μ g/L and of perfluorooctanesulfonic acid (PFOS) from 0.041 to 0.156 μ g/L. Forty percent of detectable concentrations exceeded the 2016 Health Advisory Level of 0.07 μ g/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 $P \le 0.0007$). 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?

rironmental Fate and Transport for - and Polyfluoroalkyl Substances continued



Figure 2. Conceptual site model for industrial sites.

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

AFFF is also an occupational exposure hazard with firefighters the most exposed.



PFAS are a group of chemicals that pose significant threats to human health, including pregnancy complications and cancer. They can be found in many water supplies, but have recently been found in alarming amounts at US military bases, due in part to the military's heavy use of PFAS-containing fire-fighting foam.

Fire fighter exposures should not be ignored when setting priorities for action.



Project: Firefighter Occupational Exposures (FOX) Project

Study Group: Firefighters

> Sample Collection Date: 2010 to 2011

					95% Cor Inte	nfidence rval	Se	lected F	Percentil	es		
Chemical measured	Indicates exposure to	Units	Number of people tested	Geometric mean	Lower	Upper	25th	50th	75th	95th	Detection frequency	Limit of detection (LOD)
Et-PFOSA-AcOH	EtPFOSAAcOH	ng/mL	101	0.016	0.014	0.018	<lod< td=""><td>0.016</td><td>0.023</td><td>0.060</td><td>65.3%</td><td>0.011</td></lod<>	0.016	0.023	0.060	65.3%	0.011
Me-PFOSA-AcOH	MePFOSAAcOH	ng/mL	101	0.16	0.13	0.18	0.086	0.14	0.24	0.61	100%	0.013
PFBuS	PFBuS	ng/mL	101	*	*	*	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.020</td><td>6.9%</td><td>0.02</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.020</td><td>6.9%</td><td>0.02</td></lod<></td></lod<>	<lod< td=""><td>0.020</td><td>6.9%</td><td>0.02</td></lod<>	0.020	6.9%	0.02
PFDeA	PFDeA	ng/mL	101	0.899	0.783	1.03	0.512	0.721	1.72	2.63	100%	0.032
PFDoA	PFDoA	ng/mL	101	*	*	*	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>0%</td><td>0.040</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0%</td><td>0.040</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0%</td><td>0.040</td></lod<></td></lod<>	<lod< td=""><td>0%</td><td>0.040</td></lod<>	0%	0.040
PFHpA	PFHpA	ng/mL	101	0.13	0.11	0.15	0.06	0.12	0.22	0.63	75.2%	0.059
PFHxS	PFHxS	ng/mL	101	2.26	2	2.54	1.61	2.27	3.13	4.64	100%	0.012
PFNA	PFNA	ng/mL	101	1.15	1.06	1.25	0.888	1.13	1.49	2.21	100%	0.075
PFOA	PFOA	ng/mL	101	3.75	3.37	4.17	2.96	3.86	4.89	9.54	100%	0.301
PFOS	PFOS	ng/mL	101	12.5	11.3	13.8	10.1	12.7	16.8	24.7	100%	0.083
PFOSA	PFOSA	ng/mL	101	0.032	0.027	0.037	0.019	0.029	0.050	0.151	95.0%	0.009
PFUA	PFUA	ng/mL	101	0.24	0.21	0.27	0.17	0.26	0.37	0.53	100%	0.010
							-					

We need a state strategy that looks at all PFAS Chemicals.

Why should we care about PFASs other than PFOS/PFOA?

- Many PFASs are used in AFFF and other products and identified in groundwater, sediments and soil, but won't be on 'lists' anytime soon.
 - Toxicity data and analytical standards exist for some but not all PFASs. Analytical methods (ideally, multilab validated methods) are also needed.
- Treating drinking water sources require knowledge of target contaminants (consider all PFASs as well as other chemicals present onsite) when identifying appropriate treatment technology
 - EPA 2016 Health Advisories for PFOS¹ and PFOA² have good info on treatment
 - Short-chain PFASs exhibit early breakthrough on GAC, limited removal by conventional ion exchange^{3,4}

e 1:

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

Unfortunately
"non-stick"
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breakthrough
granular
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Perfluorooctane Sulfonamide (PFOSA)ug/LPerfluorooctane Sulfonate (PFOS) - EPA PHA = 0.20 ug/Lug/LPerfluoropentanoic Acid (PFPeA)ug/LPerfluorotetradecanoic Acidug/LPerfluorotridecanoic Acid (PFUnA)ug/LPerfluorotndecanoic Acid (PFUnA)ug/LTOTAL DETECTED PFCsug/L	Perfluorononanoic Acid (PFNA)	ug/L
Perfluorooctane Sulfonate (PFOS) - EPA PHA = 0.20 ug/Lug/LPerfluoropentanoic Acid (PFPeA)ug/LPerfluorotetradecanoic Acidug/LPerfluorotridecanoic Acid (PFUnA)ug/LPerfluorotnatecanoic Acid (PFUnA)ug/LTOTAL DETECTED PFCsug/L	Perfluorooctane Sulfonamide (PFOSA)	ug/L
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Perfluorotetradecanoic Acid ug/L Perfluorotridecanoic Acid ug/L Perfluoroundecanoic Acid (PFUnA) ug/L TOTAL DETECTED PFCs ug/L	Perfluoropentanoic Acid (PFPeA)	ug/L
Perfluorotridecanoic Acid ug/L Perfluoroundecanoic Acid (PFUnA) ug/L TOTAL DETECTED PFCs ug/L	Perfluorotetradecanoic Acid	ug/L
Perfluoroundecanoic Acid (PFUnA) ug/L TOTAL DETECTED PFCs ug/L	Perfluorotridecanoic Acid	ug/L
TOTAL DETECTED PFCs ug/L	Perfluoroundecanoic Acid (PFUnA)	ug/L
	TOTAL DETECTED PFCs	ug/L

~44,	394 gal Tre	ated	~43,520 gal Treated						
INF _{AVG}	IX-EFF-1	% Leakage	INF _{AVG}	GAC-EFF-	% Leakage				
19	0.75	4.1%	17.7	3.9	22.0%				
0.26	0.0055 U		0.24	0.025	10.5%				
0.053 0	0.0053 0		0.053 0	0.0053 0					
0.049 0	0.0049 0		0.049 0	0.0049 U					
0.040 U	0.0040 U		0.040 U	0.0040 U					
0.061 U	0.0061 U		0.061 U	0.0061 U					
1.1	0.0019 U	0.2%	1.1	0.45	42.4%				
1.1	0.83	73.2%	1.3	1.3	103.4%				
0.043 U	0.0043 U		0.043 U	0.0043 U					
0.066 U	0.0066 U		0.066 U	0.0066 U					
0.057 U	0.0057 U		0.057 U	0.0057 U					
1.2	0.0036 U	0.3%	1.2	0.18	15.6%				
1.8	0.012 J	0.7%	1.8	0.81	45.4%				
21.7	0.0040 U		21.9	5.0	22.9%				
7.2	0.25	3.5%	7.3	4.4	60.5%				
11.0	0.015 J	0.1%	10.6	3.3	31.0%				
0.059 J	0.0046 U		0.064 J	0.010 J					
0.058 U	0.0058 U		0.058 U	0.0058 U					
25.7	0.0033 U		27.0	3.1	11.5%				
4.0	0.54	13.4%	4.2	3.3	79.1%				
0.052 U	0.0052 U		0.052 U	0.0052 U					
0.032 U	0.0032 U		0.032 U	0.0032 U					
0.037 U	0.0037 U		0.037 U	0.0037 U					
93.6	2.4	2.6%	94.2	25.8	27.4%				

PFAS Precursors Breakdown into the most Toxic Congener.



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

able 5. Summary of FIAS removals for various creatment processes.										
		Removal:	<10%	10-90%	> 90%			* **		
		M.W. (g/mol)	AER	COAG/ DAF	COAG/ FLOC/ SED/ G- or M-FIL	AIX	GAC	NF	RO	MnO4, O3 ClO2, Cl2, CLM, UV, UV-AOP
	PFBA	214	assumed	assumed						175.45
	PFPeA	264			10 Autor					
	PFHxA	314								1
	PFHpA	364								15
	PFOA	414		all and						
pu	PFNA	464		unknown		assumed	assumed			
mpou	PFDA	514		unknown		assumed	assumed			
3	PFBS	300								
	PFHxS	400		1.1.	and the					12.5
	PFOS	500								il locus
	FOSA	499	unknown	unknown	2 miles	unknown	assumed	unknown	assumed	unknown
	N-MeFOSAA	571	assumed	unknown		assumed	assumed	assumed		unknown
	N-EtEOSAA	585		unknown	1 inglight	assumed	assumed	assumed		unknowna

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

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



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PFAS Precursors like GAC. PFAAs like Anion Exchange Resins.

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



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PFAS Treatment Technologies for Water

Range of Practicality for PFAS Treatment Technologies



FAS treatment technologies for water

Sweden is Regulating a Sum of 11 PFAS Chemicals in Water At 90 ng/L.

Today, there exists an action limit for the sum of 11 PFAS compounds in drinking water of 90 ng/L in Sweden, provided by the National Food Agency (Livsmedelsverket 2016), including: perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, 6:2 fluorotelomer sulfonic acid (6:2 FTSA), perfluorobutanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA). This action limit is based on a potential risk for human health coming from PFASs in drinking water, for details see Livsmedelsverket (2014a). If concentrations of these 11 compounds are higher than the action limit, measures need to be taken in order to reduce them. Until

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

PFAS Levels in Human Plasma, Serum, and Breast Milk



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

How are other States Setting Drinking Water Standards?

States With Numerical PFAS Limits



Bloomberg Environment

EPA has approved over 600 NEW PFAS Chemicals for Use since 2006.

The elements ofa Rational, Comprehensive Action Plan for Chemicals Used in Commerce

Cradle to Grave Regulation would include:

- Pre-Market Review of Chemicals PRIOR to Manufacture for Toxicity, Transport, and Fate
- Protections for Society's Most Vulnerable
- A Comprehensive Monitoring Plan for Each Chemical Used to Insure No Release Occurs
- A Technological Plan for Destruction

Pandora's Box is Already Opened: What Now? • The Plan Now Would:

- Seek to reduce exposure immediately, especially to the most vulnerable.
- Seek to prevent further releases from future actions
- Seek to prevent media transfer from the regulated media to the unregulated media.
- Seek better analytics in the near term, and seek to know the "whole problem" at some definite point in the future.
- Seek an ultimate destruction (not disposal) technology that will break the chemicals apart.

So what do We do?

- We need to use the best analytics we have now and generate occurrence data for drinking water....NOW.
- We need to push the analytics for a total PFAS Assay for all media using our unique state authorities in AB 289.
- We need an exposure reduction strategy that focuses on dramatic exposure reduction measures in the near term: food sources, drinking water, and home and personal care products.

What we do now.... Continued.

- We need to use our relationship with the National Academy of Sciences to help identify destruction technologies.
- We need to identify remediation technologies for drinking water, and destruction technologies for their residuals.
- We need to stop the flow of these highly toxic chemicals which are also very soluble into our state.

California Needs a Comprehensive Plan on PFAS to Protect it's **Residents and** Resources.

