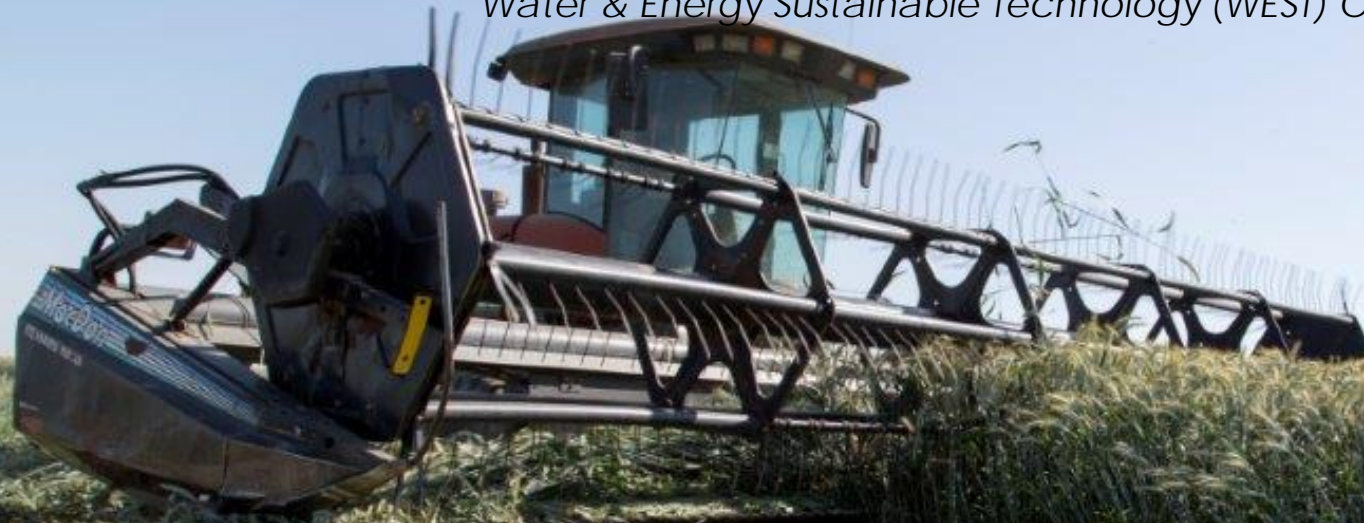


FUNDAMENTALS OF PERFLUORINATED COMPOUNDS

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Water & Energy Sustainable Technology (WEST) Center



Biosolids: Beyond a Movement
Northwest Biosolids
Portland, Oregon
October 15-16,, 2017



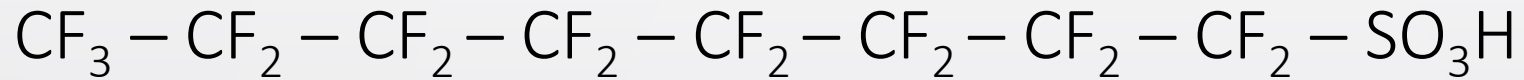
PERFLUORINATED COMPOUNDS (PFCs)

- Fully fluorinated long chain organic compounds
- Family of anthropogenic chemicals used for decades to make products resistant to heat, oil stains, grease and water
- Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) most prevalent PFCs in the U.S.
- Regarded by EPA as an “emerging contaminant”

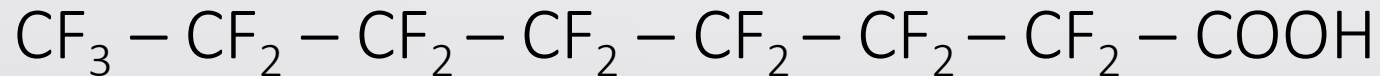


Structure of PFOS and PFOA

PFOS



PFOA



Long carbon chain fluorinated results in unique lipid and water repellent characteristics



Characteristics of PFOS and PFOA

- Persistent in the environment, resistant to most microbial degradation processes
- Found in soil, sediments, and water
- Soluble and can migrate through soils
- All people in the U.S. thought to have PFCs in their blood
- Can stay within human body for many years



Household Exposure to PFCs

- Textiles
- Carpets
- Cleaning agents
- Leather
- Baking and sandwich papers
- Ski waxes
- Gloves
- Household dust

PFOS voluntarily phased out of production in the U.S. between 2000 and 2002

PFOA phased out by 8 major companies in the U.S. in 2006



Health Effects of PFOS and PFOA

- No consistent evidence of adverse human health effects
- BUT, potential adverse health effects cannot be excluded due to laboratory studies on rats and mice showing changes in liver and thyroid activity and reproductive problems
- No conclusive evidence that PFOS or PFOA cause any specific illness including cancer
- BUT, International Agency for Cancer Research (IACR) has classified PFOA as a possible carcinogen, but not PFOS

CONCLUSION: health effects unclear



Health Effects of PFOS and PFOA

- Tolerable daily intake (TDI)

PFOS = 0.02 ug/kg body weight

PFOA = 0.16 ug/kg body weight

- EPA Health Advisory Levels in Drinking Water

- January 2009

PFOS = 200 ng/L (ppt)

PFOA = 400 ng/L (ppt)

- November 2016

Combined PFOS + PFOA not to exceed 70 ng/L (ppt)

Regulatory Standards for PFOA and PFOS in drinking water. Parts per **trillion**.

Jurisdiction		PFOA (ppt)	PFOS (ppt)	Notes
Advisory or Regulatory Standard				
U.S. EPA, 2016	Advisory		70	For combined
New Hampshire, 2016, AGWQ	Standard		70	For combined
Vermont, 2016	Standard	20	20	
Australia, January 2017 interim drinking water guidance	Advisory	5,000	500 (including PFHxS)	
Australia, April 2017 final drinking water guidance	Advisory	70	560 (including PFHxS)	
Canada, proposed June 2016	Standard	200	600	
Michigan, non-cancer values, 2014		420	11	
Minnesota drinking water				
(as of 2016)	Standard	300	300	PFBA & PFBS = 7000
(as of 2017)	Advisory	35	27	Adopted 5/2017

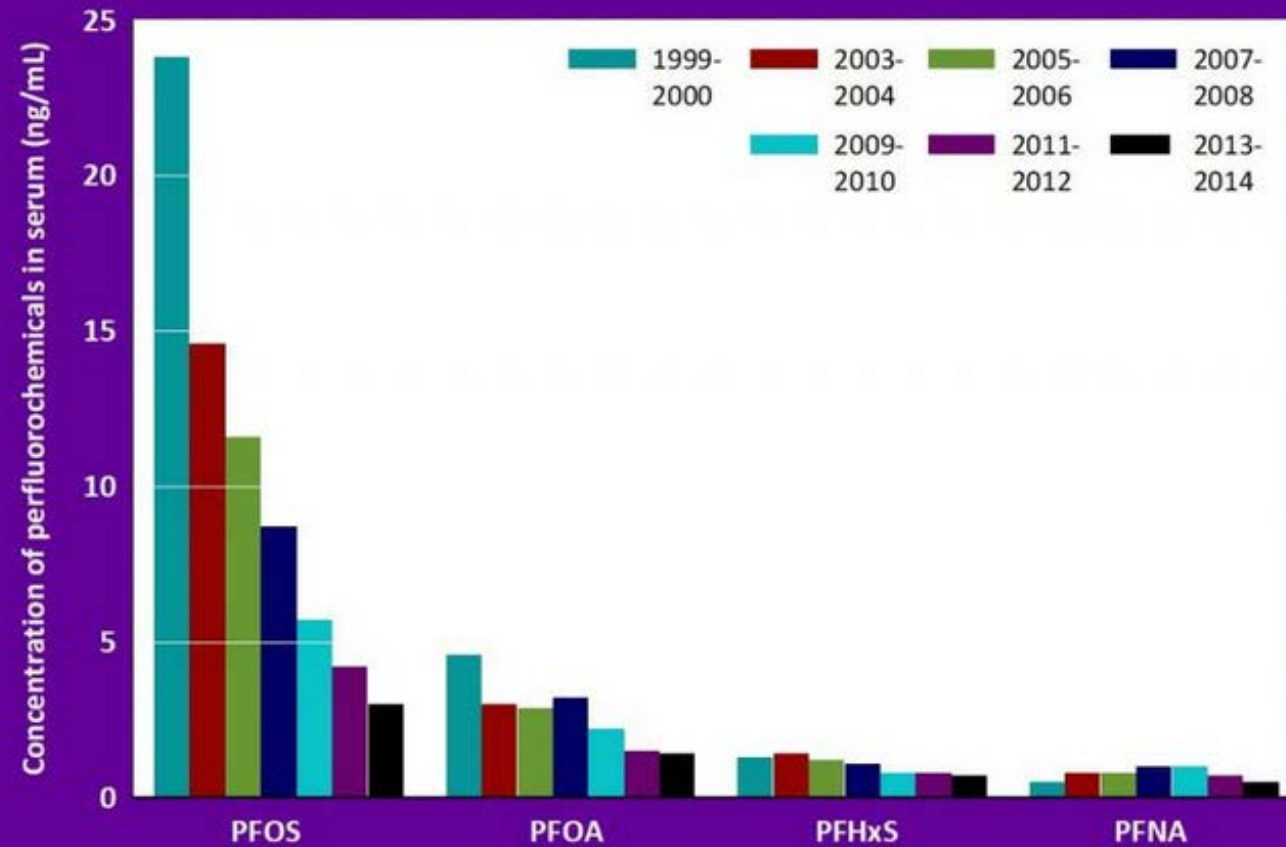
Soil Screening Levels for PFOA and PFOS. Parts per **billion**.

Jurisdiction	PFOA (ppb)	PFOS (ppb)	Notes
Soil			
Australia, 2017 – soil screening level for 99% species protection	650	6,600	
Minnesota soil reference value, in effect in 2012	2100	2100	
NH DES Soil Screening Level	500	None	Based on risk from dermal exposure and ingestion
EPA Region 4 residential soil screening level (2009)	16000	6000	

PFOA and PFOS levels measured in various media compared to current advisory and regulatory levels. Parts per **billion**.

Jurisdiction	PFOA (ppb)	PFOS (ppb)	Notes
Biosolids & Residuals			
Regulatory standards	None	None	
Sampling of U.S. biosolids, 2001 (Venkatesen and Halden, 2013)	34	403	
A northern New England biosolids compost, 2017	8.3		
NH land applied solids, 2017 (n=20)	2.3	5.3	Mean (includes 17 wastewater biosolids, 2 paper mill residuals, & 1 water treatment residual)
Northeast paper mill residuals	1.6	25	
Other media			
Household organic waste compost	6 (median) 34 – 35 (range)		All PFAS combined
Dust in U.S. daycare centers, median values (Strynar and Lindstrom, 2008)	142	201	
Human blood, U.S. population 1999 average (CDC NHANES)	5	30	
Human blood, U.S. population 2012 average (CDC NHANES)	2	6	

Perfluorochemicals in women ages 16 to 49 years: Median concentrations in blood serum, 1999-2014



Data: Centers for Disease Control and Prevention, National Center for Health Statistics and National Center for Environmental Health, National Health and Nutrition Examination Survey

Note: To reflect exposures to women who are pregnant or may become pregnant, the estimates are adjusted for the probability (by age and race/ethnicity) that a woman gives birth.


America's Children and the Environment, Third Edition, Updated August 2017

PFCs and BIOSOLIDS



PFC Exposure from Biosolids

- Direct exposure (minimal)
- Indirect exposure
 - drinking water
 - plant/animal uptake
- Bioaccumulation



Industrially Contaminated Biosolids Used for Land Application (Lindstrom, 2011)

- Land application in Decatur, Alabama, 1995-2008
- Biosolids contaminated by effluent from industries producing PFC materials, e.g., 3M Company
- 34,000 dry metric tons applied to \approx 2000 ha of agricultural fields (17 metric ton/ha)
- Surface and ground waters contaminated with PFOA at levels above EPA Health Advisory Levels

This led to scrutiny of PFCs

Bioaccumulation of PFCs by Earthworms (Rich et al., 2015, Chris Higgins – coauthor)

- Lab study
- Soil contaminated with PFCs
 - Nalgene 1 L bottles
- 5 worms added to each bottle
 - Industrially contaminated biosolids
 - PFOS in soil = 243 ng/g (ppb)
- Incubated for 28 days

RESULT

- Bioaccumulation of PFCs

QUESTION: Is this realistic?

Occurrence and Fate of PFCs in Soil Following Land Application of Municipal Biosolids (Sepulvado et al., 2011, Chris Higgins, co-author)

- Worst case scenario
 - 100 years of agronomic biosolids applied within 33 years
- PFCs found at depths up to 120 cm (40")
- Little degradation of PFCs

RESULT

- PFCs persistent with limited mobility

Uptake of PFCs into Edible Crops

(Blaine et al., 2013, Chris Higgins – co-author)

Greenhouse studies

- Soil contaminated with PFCs
 - Industrially contaminated biosolids
 - Biosolids applied at 10x agronomic rate
- Pot study!!
 - Lettuce grown and shown to take up PFCs
 - PFOS levels \approx 100 ng/g (ppb)
- Spiked studies show uptake of PFCs

Field Studies

- Municipal and industrial biosolids applied up to 10x agronomic rate
 - maximum PFOS soil concentrations \approx 14 ng/g (ppb)
 - PFOS in corn grain below the level of detection

Author quote:

“... crops grown on soils amended with municipal biosolids (not impacted by PFAA industries are unlikely to be a primary source of PFC exposure.”

**Comparison of 2015 Unfiltered Groundwater Concentrations
at Green Acres Farm (GAF) to Federal Standards (µg/L)**

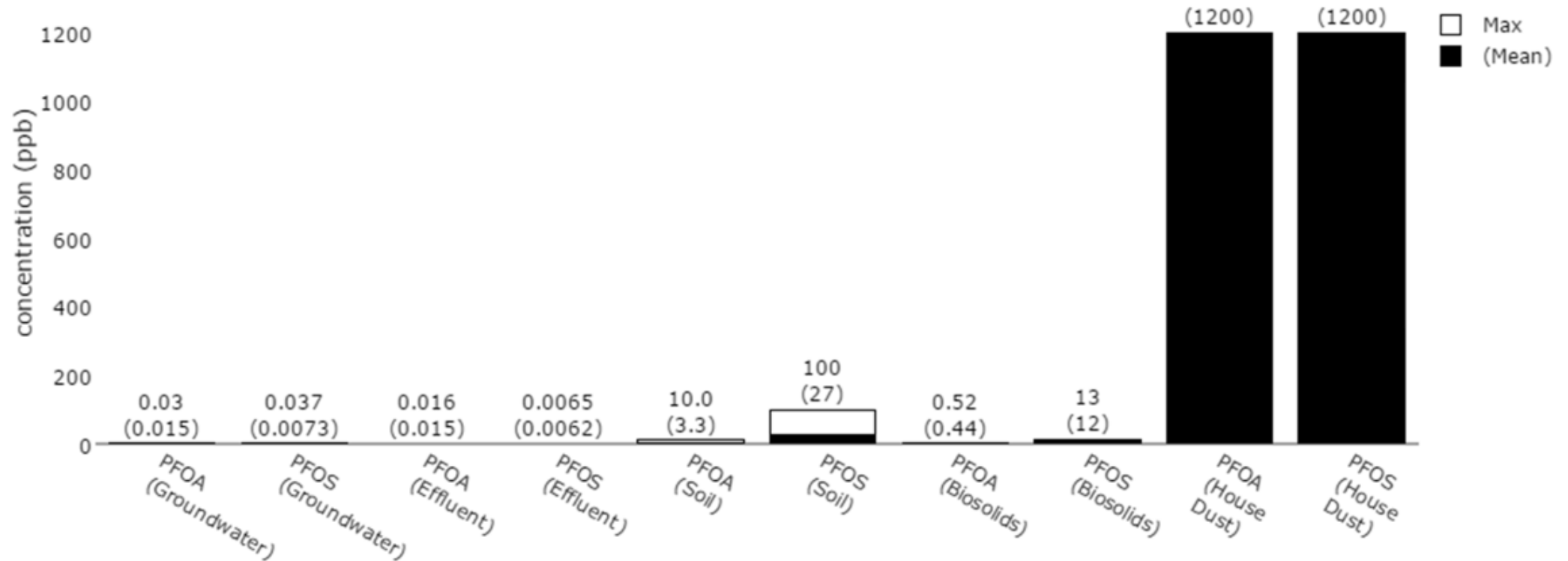
Analyte	GAF Groundwater Samples			Federal Drinking Water Standards
	Field	Depth to Groundwater (feet)	Mean Concentration	
PFOS	7-1	71.5	0.037	0.2
	7-2	61.72	0.0029	
	1-4	49	0.0021	
	1-7	55	0.002	
PFOA	7-1	71.5	0.022	0.4
	7-2	61.72	0.00205	
	1-4	49	0.0115	
	1-7	55	0.0295	

Comparison of 2015 Soil Concentrations at Green Acres Farm (GAF) to Soil Regulatory Values (mg/kg)

Analyte	GAF Soil Concentrations			Soil Regulatory Values				
				Residential Soil			Industrial Soil	
	Sampling Depth (feet)	Maximum (Max)	Mean	USEPA Regional SL	CA DTSC SL	USEPA Regional SL Calculator Results	USEPA Regional SL	CA DTSC SL
Perfluorobutane Sulfonate (PFBS)	1	0.0044	0.0018	1,600	--	--	23,000	--
	2	0.0024	0.0009					
	3	0.0032	0.0010					
	>3	--	--					
Perfluorooctane Sulfonate (PFOS)	1	0.10	0.061	6	--	2.35	--	--
	2	0.027	0.015					
	3	0.021	0.008					
	>3	0.026	0.004					
Perfluorooctanoic Acid (PFOA)	1	0.032	0.013	16	--	1.56	--	--
	2	0.016	0.007					
	3	0.017	0.007					
	>3	0.031	0.003					

KERN COUNTY CASE

PFOA and PFOS in effluent, soil, and biosolids measured at Green Acres Farm, 2015, compared with PFOA and PFOS concentrations in household dust*



*Household dust measurements from Trudel et al. *Risk Analysis*, Vol. 28, No. 2, 2008

CLASSIC RESEARCH MISTAKES



Research Mistake #1:

Pot studies instead of field studies

Research Mistake #2:

10x agronomic rate is not the same as 10 years at 1x rate

Research Mistake #3:

Spiked chemicals not the same as chemicals within biosolids



SUMMARY

- PFCs in the environment ubiquitous but will decrease over time as legacy products disappear
- PFCs in blood of all U.S. population but have been decreasing since the early 2000s
- PFC exposure from land application of biosolids is minimal
- Other than biosolids contaminated with industrial sources of PFCs, all PFCs in biosolids is the result of human excretion