Poly- and Per-fluoroalkyl Substances (PFASs): What's the Hoopla?

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Western Coalition of Arid States (WESTCAS) 2019 Fall Conference October 23, 2019 Westward Look Wyndham Grand Resort - Tucson, AZ



Colorado School of Mines?

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State University, Engineering and Science BS, MS, PhD 4500 BS, 1600 Graduate Top Research School per Faculty



Team at Colorado School of Mines

- Chris Higgins Environmental Chemistry and Transport
 - These are mostly Chris' slides
- John McCray Contaminant transport & Remediation
- Chris Bellona Water treatment and remediation
- Tissa Illangsekare Transport
- Timm Strathmann Chemistry and Treatment
- Jennifer Fields (Oregon State)
- Craig Benson (Univ. Virginia)
- Charles Schaeffer (CDM Smith)
- Jeff Silva (GSI)

May 19, 2016





Emily Donovan, co-founder of Clean House Subcommittee on Environme (House E&C)

THE TRUTH HAS A MAN ON THE INSIDE.





SCREENPLAY BY MARIO CORREA AND MATTHEW MICHAEL CARNAHAN DIRECTED BY TODD HAYNES

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Change Region ¥

customers advised not to ical contamination

LIVE TV Edition V

er is dumping 12,000 y. Here's why



What's this all about?

- What are PFASs?
- Why are PFASs an issue for environmental engineering and sciences?
- What are the future challenges?

More than 95 percent of the U.S. population has PFAS in their bodies, according to the <u>Centers for Disease</u> <u>Control and</u> <u>Prevention</u> (CDC).



Feb. 14, 2019, the EPA unveiled its delayed <u>Nationwide</u> <u>Per- and</u> <u>Polyfluoroalkyl</u> <u>Substances Action</u> Plan.

Perfluorinated vs. Polyfluorinated precursors



<u>N-et</u>hyl Per<u>f</u>luoro<u>o</u>ctane <u>s</u>ulfonamido<u>e</u>thanol (N-EtFOSE)



Most *per-fluorinated* substances are perfluoroalkyl acids (PFAAs).

Perfluoroalkyl acids (PFAAs)



- PFAAs Fluorinated chemicals that repel both oil and water
- PFAA-based precursors (i.e., <u>poly</u>fluorinated substances) used in coatings for textiles and paper packaging products, fire-fighting foams, etc.
- Persistent, Bioaccumulative, and Toxic (PBT)
- Widely detected in wildlife and humans
- Relatively mobile and yet bioaccumulative

Polyfluorinated substances form PFAAs over time



<u>p</u>er<u>f</u>luoro<u>o</u>ctane <u>s</u>ulfonate <u>N-et</u>hyl per<u>f</u>luoro<u>o</u>ctane <u>s</u>ulfonamido<u>e</u>thanol N-E**PFOS**E

<u>Perfluoroo</u>ctanoic <u>a</u>cid <u>8:2 f</u>luoro<u>t</u>elomer <u>S</u>ulfon<u>a</u>mido <u>B</u>etaine

8:2**PFCS**ABB

Electrochemical fluorination (ECF)

Fluorotelomerization (FT)



Long-chain PFAAs generally discontinued: short-chain production ongoing



Sources of PFASs

- Consumer products
 - Paper packaging, fabric treatments \rightarrow landfills and wastewater (\rightarrow biosolids, effluent)
- Industrial/Infrastructure products
 - Film coatings, surface treatments \rightarrow stormwater and surface waters

Industrial processes

- Chrome plating facilities \rightarrow industrial wastewater (\rightarrow biosolids, effluent) and surface/ground waters
- Polymer manufacturing \rightarrow industrial wastewater (\rightarrow biosolids, effluent) and surface/ground waters
- Aqueous film-forming foam (AFFF)
 - Fire training facilities, military sites, airports, fuel depots, local fire stations \rightarrow surface/ground waters

Used since the 1950s and still in use today*

A little AFFF goes a long way



<u>One</u> 5 gallon bucket of historical 3M Lightwater AFFF has enough PFOS to contaminate a 27,000person town's annual water supply to 70 ng/L

<u>One</u> U.S. Olympic-sized swimming pool filled with 3M Lightwater (AFFF) would have enough PFOS in it to contaminate ~7 years worth of the drinking water supply for the entire U.S. population

Potential for AFFF releases is large



Why care? PFOS and PFOA Toxicology

- Non-cancer effects^{1,2}
 - EPA reference doses (RfD for PFOA and PFOS (non-cancer hazard only)
 - PFOS: 0.00002 mg/kg*day (reduced birth weight)
 - PFOA: 0.00002 mg/kg*day (developmental effects in bones, accelerated puberty)
- Immunotoxicity potential^{3,4}
- Potential carcinogenic properties⁵
 - "Suggestive" for both (EPA) and "Possibly" for PFOA (International Agency for Research on Cancer)
 - Risk-based drinking water threshold for cancer endpoint higher (less conservative) than non-cancer endpoint
- Many epidemiology studies (used qualitatively in support of RfDs)^{6,7}
- Very limited information available for other PFASs

¹Lau, 2012. Clinical and Environmental Toxicology, Experientia Supplementum 101; ²ATSDR, 2015. Draft Toxicological Profile for Perfluoroalkyls; ³Grandjean et al., 2012. JAMA; ⁴Granum et al., 2013. J Immunotox.; ⁵USEPA, 2016. Drinking Water Health Advisories for PFOA and PFOS; ⁶C8 Science Panel (<u>http://www.c8sciencepanel.org</u>); ⁷ Olsen et al., 2009. Reproductive Toxicology 27:212-230

Slide content courtesy of ESTCP Project ER-201574-T2. Full FAQ presentation available at https://youtu.be/lyzSoEF792E

Drinking water advisory levels are coming down



Slide content courtesy of D.MacIntosh, Environmental Health & Engineering

PFAS Environmental Behavior





The Complex Challenges of PFASs



The Complex Challenges of PFASs



The Complex Challenges of PFASs



Ground Water Transport



PFAS - does not sorb to soil, does not degrade

TCE – sorbs to soil, degrades near source

BTEX - sorbs to soil, degrades away from source

PAH – sorbs strong to soil, does not degrade as much

Vadose Zone Can Act as a Long-Term Source



PFAS may be relatively immobile in deep, arid vadose zones



PFAS partition to air-water interface and greatly slows transport

Human Exposure to PFASs



Bioaccumulation Patterns

accumulate in the living organism



Blaine et al., 2014. ES&T.

Water Treatment Options for PFASs

Most traditional water treatment tech does not remove...

Horsham Township Council members inspect new water filter

A press release from Horsham Township Mar 29, 2017 Updated Mar 30, 2017



Many plants installing Granular Activated Carbon (GAC) or Ion Exchange (IX).

Research suggests that GAC and IX work well for removing long-chain PFAS, but not the shorter chain PFAS.

HORSHAM >> Horsham Township Council members conducted their inspection of the newly constructed granular activated carbon filter (GAC) at Well 26. They were accompanied by Horsham Water and Sewer Authority (HWSA) and township staff.

The new GAC filter will remove PFOA and PFOS from the water. Well 26 is back in service and providing filtered water to the community.

"I am very pleased that Well 26 is now providing safe, filtered...

Reverse Osmosis shown to be effective for all PFAS

Treatment is Costly

- U.S. Department of Defense
 - Initial \$2 billion (over 10 years) will likely be significantly exceeded
- Based on *limited* national data, the AWWA recently estimated:
 - \$23 48 billion in capital costs for PFOS and PFOS
 - \$0.46 to 4.8 billion annual O&M for for PFOS and PFOA

Most importantly:

- True scope of contamination still unknown
 - Soils are likely major reservoirs of PFAS mass
 - It may be decades before some water supplies are impacted
- Treatment targets are decreasing



Current and Future Challenges

- Understanding of transport in multiphase, mixed chemical systems is still naïve.
- How can we reduce human and ecological exposure?
- How can we clean up sites?
 - Can/should we cleanup everywhere?
- How do we communicate uncertainties to the public?
- Are policy and regulatory frameworks sufficient?



What are we working on at Mines?

- U.S. DoD Analysis of PFAS
- U.S. DoD Sorption and Partitioning behavior
- U.S. DoD Transport in Ground water
- U.S. DoD Remediation
- U.S. DoD Transport and Sources in Vadose Zone

Center for Disease Control – Fountain CO, backtracking exposures to current and former residents

Thank you!

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US EPA Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA

https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass

... persistent in the environment; bioaccumulative in wildlife and humans; and toxic to laboratory animals and wildlife, producing reproductive, developmental, and systemic effects in laboratory tests.

PFAS comprise two sub-categories:

- PFCAs: perfluoroalkyl carboxylic acids with 8 or more carbons including PFOA, and
- PFSAs: perfluoroalkane sulfonates with 6 or more carbons, including
 - perfluorooctane sulfonic acid (PFOS)
 - perfluorohexane sulfonic acid (PFHxS)