Per Fluoroalkyl Substances (PFAS)
What They Are,
Why You Should Care,
and What's Being Done

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Today's Presentation

What are PFAS compounds and where do they come from?

How are people exposed to PFAS?

Where do we find PFAS in the environment?

What are the health effects of PFAS?

How are PFAS being regulated by EPA and other agencies?

What are the sampling and analysis challenges of PFAS?

How can PFAS in the environment be cleaned up?

PER- AND POLY-FLUOROALKYL SUBSTANCES

PFAS – New Class of Emerging Contaminant

- An environmental Emerging Contaminant (EC) is a chemical that:
  - May pose a potential human health or environmental risk
  - Does not have (widely accepted) regulatory standards
- US chemical regulatory system doesn't always require significant proof of safety prior to widespread use
  - ECs aren't necessarily rare or unique chemicals, key issue is that they lack toxicity and/or regulatory criteria
- DoD, industrial, and commercial uses can result in large environmental releases, disposals, and spills
- Consumer products and applications, pharmaceuticals and drug products, munitions and propellants

What are PFAS?

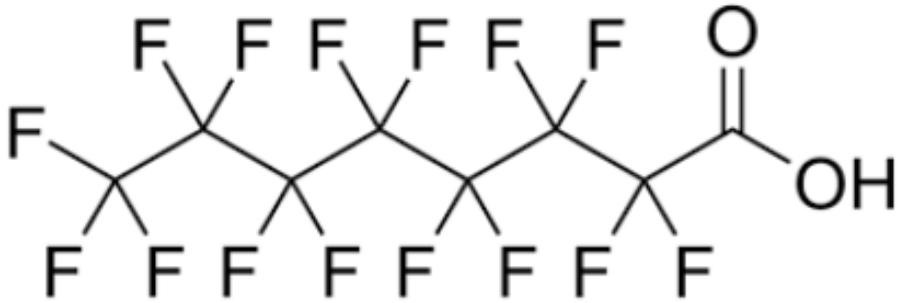
- PFAS = Per or poly fluorinated alkyl substances, the term given to a broad group of fluorinated chemicals
- Over 5,000 individual PFAS chemicals; complex mixtures
- PFOS and PFOA are the most well studied – “legacy PFAs”
  - 8 carbon atoms each, fully fluorinated (hence the term “per”)
  - No longer in widespread production or use, but are major components of groundwater contamination due to historical use
- PFAS are bioaccumulative and persistent in the environment, are soluble in water, and can migrate long distances in groundwater
- Main chemical in AFFF, aqueous film forming foam (aka, fire fighting foam) – used for aircraft and petroleum hydrocarbon fires

Example Use for Aircraft Fires at Military Bases

Chemical Structures of PFOS and PFOA

PFOS
Perfluorooctane Sulfonate
Formula: C8HF17O3S

PFOA
Perfluorooctanoic Acid
Formula: C8HF15O2



Widespread Uses of PFAS

- Managing and extinguishing petroleum based fires
- Airports, refineries, fire training areas, fire trucks, military
- Chrome and copper plating and fume suppression
- Anti-stick cookware and kitchenware
- Water repellants for fabric, carpeting, clothing and shoes
- Waterproofing and grease resistance for paper products
- Commercial and industrial cleaning products
- Oil and gas industry - as surfactants to enhance recovery in oil or gas wells and as evaporation inhibitors for petroleum storage

How are Humans Exposed to PFAS?

- Primarily through drinking water, in particular from using private wells and bores accessing contaminated groundwater
  - Adjacent to military bases
  - Near to airports or other industrial facilities with a history of PFAS use and release
  - From landfilled waste materials leaching into groundwater
- Secondary exposure from consumer products and food
  - Cookware, water repellent clothing, carpeting
  - Consumption of animals and plants containing PFAS
- Occupational exposures for some groups
  - Manufacturing, transportation, other industries

The Many Challenges of Managing PFAS Human Health Toxicology and Risk

- While toxicology is reasonably defined for PFOA/PFOS, less so for other compounds
  - Will agencies move towards single PFAS toxicity value?
    - Currently chemical by chemical for a small number of compounds
  - Uncertainties due to limited knowledge of toxicity of most PFAS chemicals
- Regulatory toxicity criteria based on animal studies, and also consider:
  - Epidemiology findings in highly exposed human populations
  - Differences in biological half life in animals and humans
- Use of pharmacokinetic modeling to adjust animal-to-human doses
- Concerns over risk from PFAS in the food chain and dietary exposures
- Significance of background exposure to PFAS in commercial products

What are the Toxic Effects Associated with PFAS?

- Organs most commonly associated with PFAS toxicity:
  - Liver: enzyme release into bloodstream, changes in liver weight
  - Reproduction and Development: decreased maternal weight gain and fetal body weight
  - Immune System: delayed response to vaccine based stimuli
  - Elevated blood cholesterol

Most of the observed effects in animals considered relevant to humans

- Mechanism of action of toxicity not clear – effects are generally non-specific
- Significant difference in how animals eliminate PFAS from their system
  - Half life – measured in days in animals, but years in humans (clearance rates)
  - Remains in humans for much longer than in animals
  - Presumably due to differences in protein binding, but not totally clear yet

Bioaccumulation and Biomagnification

- Bioaccumulation occurs when chemical levels build up and remain in the body for extended periods of time
  - Intake rates >> outflow rates (PFAS excreted primary by the kidneys)
  - BA occurs in a single trophic level (i.e., not food chain)
- PFAS aren't lipophilic, rather they bind to the albumin molecule, a protein widely distributed throughout the body
  - "Fatty Acid Binding Protein", high levels naturally present in the liver
  - Slow clearance rate from humans compared to animals

Biomagnification is a food chain phenomenon, when successive trophic levels build up PFAS from ingestion of lower trophic level items

Potential Carcinogenicity of PFAS

Australian Government

Department of Health

CHIEF MEDICAL OFFICER

MEDIA RELEASE

7 May 2018

EXPERT HEALTH PANEL'S INDEPENDENT PFAS ADVICE

An independent expert health panel established by the Australian Government has concluded there is mostly limited, or in some cases no evidence, that human exposure to PFAS is linked with human disease. Importantly, the panel concluded there is "no current evidence that suggests an increase in overall cancer risk".

US EPA (2016)

there is equivocal evidence that PFOA exposure might be associated with an increased risk for cancer from the human epidemiology database and animal studies.

In the case of PFOS, the existing evidence does not support a strong correlation between the tumor incidence and dose to justify a quantitative assessment.

How are PFAS Human Health Risks Evaluated?

- In the US, we aren't doing many site-related PFAS risk assessments
  - "Risks" primarily evaluated by comparing to drinking water health advisory levels of 70 ng/L for PFOA and PFOS
- Rudimentary screening level approach, tells us little about actual risk
  - CERCLA-style multipathway risk assessments that consider soil, air, food exposure aren't widely done
- Most significant risks likely limited to locations around PFAS release sites like airports, military bases, manufacturing areas

As a result, we really don't know much about multi-pathway human health risks from PFAS mixtures, and even less about ecological risk

"Don't eat deer in part of Oscoda, Michigan due to PFAS chemical contamination"

- *Lansing* — Hunters should not eat deer taken from parts of Oscoda Township after toxic chemicals were found in one deer. A "do-not-eat" advisory for deer taken near Clark's Marsh was issued by the Michigan departments of Natural Resources and Health and Humans Services, after one of 20 deer tested at 547 ppb for PFOS.
  - The test is almost double the action level of 300 ppb, Michigan's do-not-eat advisories for fish. A do-not-eat fish advisory also remains in place for the area around Clark's Marsh.
- PFAS are in Class B firefighting foam that was used at Wurtsmith Air Force Base and other sites in Michigan. The assumption is that the deer consumed of water from contaminated waterways.

https://www.detroitnews.com/story/news/local/michigan/2018/10/19/pfas-behind-do-not-eat-advisory-deer-oscoda/1695220002/

Biosolids as a PFAS Source of Milk Contamination

- A Maine dairy farmer discovered in 2016 that his cows were producing tainted milk has threatened to shut down a century-old family business. Tests tests found high levels of PFAS in milk, soil, hay, and cow manure.
  - Maine public health officials said in 2017 that milk with PFOS exceeding 210 parts per trillion should be considered “adulterated” and banned from sale. So far, this ban has only affected one farm, whose milk had levels as high as 1,420 ppt.
- Concerns that using biosolids, or nutrient-rich sewage from municipal utilities, as fertilizers have inadvertently contaminated the land with PFAS.
- State regulators and health experts are investigating whether the contamination could reflect a much broader problem for farms that used similar methods to fertilize their land.

https://www.reuters.com/article/us-usa-dairy-chemicals/the-curious-case-of-tainted-milk-from-a-maine-dairy-farm-idUSKCN1R01AJ

PFAS Update: Colorado Springs-Area Residents Have Elevated Levels of Water Contaminants

- Blood testing of residents in three communities south of Colorado Springs showed they had high levels of toxic chemicals believed to stem from past use of firefighting foam at Peterson AFB
- For more than three years after news reports revealed contamination of drinking water, residents have been left largely on their own to deal with possible health effects
- Initial Air Force studies found that firefighting foam used at Peterson contaminated water and soil at levels more than 1,000 times higher than a EPA health advisory limit.

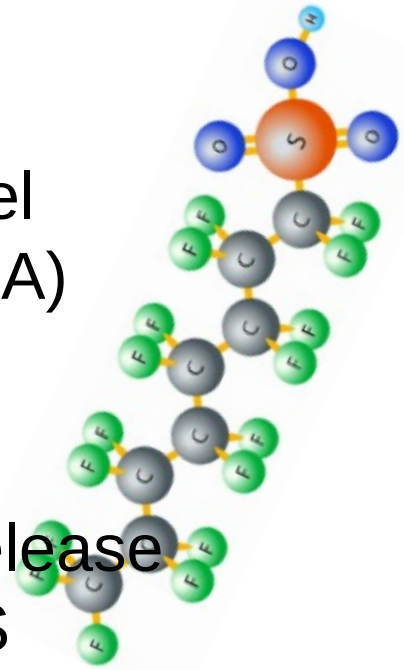
What do Blood (Plasma) Levels Mean in Regards to Human Health?

- Mostly what it tells us is whether a person has been exposed to a significant PFAS source – but doesn't identify that source
- Epidemiology has not identified a clear dose-response pattern for most toxicity endpoints in exposed human populations
- If blood levels between two similar populations are different, it may be possible to track down what is contributing to exposure
- Public health agencies should ensure proper information is provided to provide perspective
  - Managing expectations and risk communication are key steps

US EPA PFAS Management Strategy to Date

- Prepared Health Advisory (HA) levels for PFOA and PFOS in drinking water at 70 ng/L (either separately or combined)
- Has not yet formally identified PFAS as a “hazardous substance(s)”
- Has not developed promulgated Maximum Contaminant Levels for PFAS under the Safe Drinking Water Act
- Non-cancer toxicity criteria available for PFOA, PFOS, and several “GenX” chemicals
- Risk-based screening values for soil, surface water, and other media not currently available
- Recently announced PFAS “Action Plan” roadmap for EPA PFAS assessment program

EPA PFAS action plan - February 2019



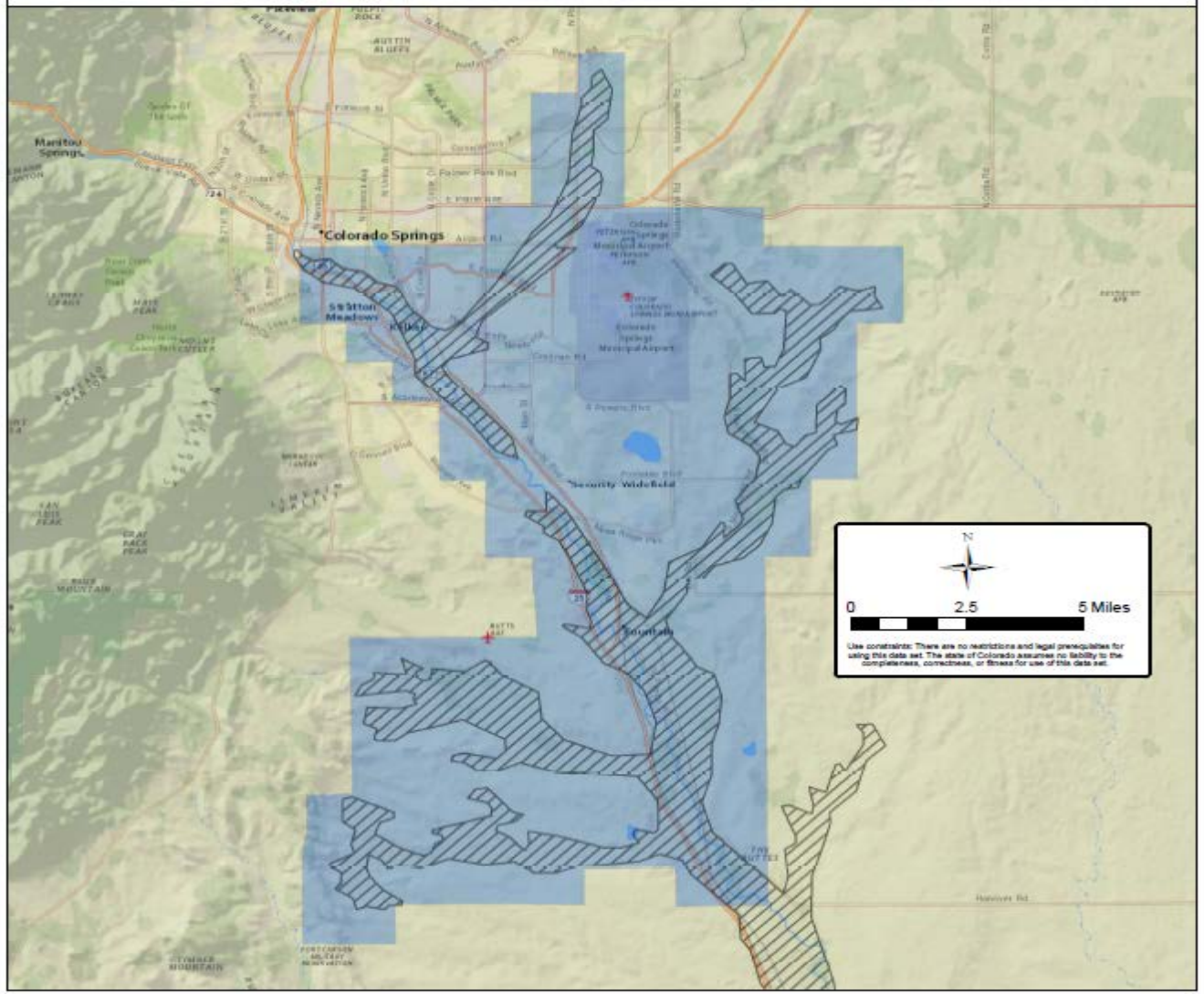
- USEPA moving forward with the Maximum Contaminant Level (MCL) process outlined in the Safe Drinking Water Act (SWDA) for:
  - PFOS and PFOA
- Considering the addition of PFAS chemicals to the Toxics Release Inventory (TRI) and rules to prohibit the uses of certain PFAS
- Continue strengthening enforcement authorities and clarifying cleanup strategies through actions such as designating PFOA and PFOS as hazardous substances and developing interim groundwater cleanup values
- Enhancing the way in which agencies communicate about PFAS

Human Health Guidelines – Drinking water

Note- Some North American criteria are enforceable at this time

Jurisdiction	PFOA (µg/L)	PFOS (µg/L)	Year
US EPA	PFOA + PFOS 0.07		2016
Delaware	PFOA + PFOS 0.07		2016
California	0.014	0.013	2018
Massachusetts	Sum of 5 PFAS 0.07		2018
Michigan	PFOA + PFOS 0.07		2017
Minnesota	0.035	0.027	2017
New Jersey	0.014	0.013	2018
Vermont	Sum of 5 PFAS 0.02		2018
Australia	0.56	0.07	2017
Canada	0.2	0.6	2018
Germany	0.3	0.3	2006
Netherlands	-	0.53	2011
Sweden	Sum of mix of PFASs 0.09		2016
UK	0.3	0.3	2009

Proposed PFOS / PFOA Site Specific Standard Boundary in Central El Paso County.



Legend

- Unconfined and Alluvial Aquifers (Tweto, 1979)
- Proposed PFOS / PFOA Site Specific Standard Boundary

COLORADO
Department of Public Health & Environment

CDPHE is taking a stepwise approach to regulating these compounds

PFOA and PFOS Hazardous Constituent Listing: On February 20, 2018, the Solid and Hazardous Waste Commission listed PFOA and PFOS as Hazardous Constituents in Colorado Hazardous Waste Regulation. This listing applies statewide …

Assess the need for statewide standards: Based on continued evaluation of the scope of perfluorinated compounds issues across the state, we continue to assess the need for statewide standards associated with PFOA, PFOS, and other perfluorinated compounds.

PFAS Contamination Management Strategies

- Regulated entities (companies, DoD, municipalities) may be forced to do more comprehensive site investigations and enter into discussions with agencies about risk management options
  - Remediation, land use controls, on-site containment, risk reduction strategies
- Are treatment technologies able to attain regulatory standards?
- Where possible, less-toxic substitutes get identified and used
- Regulatory criteria get developed at the state and federal level
  - Minimize inconsistent standard setting
  - Implement risk-based approach to site cleanup

Other PFAS Issues to Manage

- PFAS in waste water – impacts to treatment facilities
- PFAS in commercial and municipal waste and trash
- Regulatory acceptance criteria for landfill disposal
- Treatment, storage and disposal (TSD) facilities
- Remediation wastes (spent GAC, resins, etc)
  - After treatment, concentrated material will remain
- Investigation derived waste (IDW)
- Surface water transport – not much studied yet
- New “GenX” PFAS compounds may not solve the problem

Future Challenges for PFAS

- Will regulators consider revisions to cleanup values if future studies indicate that PFAS is more or less
  - toxic to humans than currently understood?
- Can we get past using Screening Levels to make all decisions and use a site-specific risk-based approach?
- Exposures have been ongoing in places for decades. Can data from epi studies be used to counterweight animal data?
- Given that PFAS risks appear modest at the general population level when compared to many other societal risks (e.g., lead contamination, opiates)
  - will it be possible to provide balance and perspective to public policy and risk-based decision making?

PFAS Regulatory Management

Unclear if/when US EPA will develop and promulgate primary drinking water standards (MCLs) for PFAS compounds

- Currently EPA has Health Advisory values for several PFAS

State health agencies are developing their own drinking water standards

Fish and game advisories being recommended for some locations

Ecological screening risk values being developed

Different countries take different approaches to evaluating PFAS

More Questions – Contact:

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PFAS Sampling challenges – Avoiding accidental contamination

Prohibited Items	Acceptable Items
Field Equipment	
Teflon® containing materials (tubing, bladders, o-rings, caps)	High-density polyethylene (HDPE) materials
Low density polyethylene (LDPE) materials	Acetate Liners
	Silicon Tubing
Waterproof field books	Loose paper (non-waterproof)
Plastic clipboards, binders, or spiral hard cover notebooks	Metal field clipboards or with Masonite
Post-It Notes®, Sharpies®	Ball point pens
Chemical (blue) ice packs	Regular ice
Field Clothing and PPE	
New cotton clothing or synthetic water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™	Well-laundered clothing made of natural fibers (preferable cotton) washed at least 6 times since purchase
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC (PVC over boots over leather steel-toe safety boots are acceptable*)
Tyvek®	Powder-free nitrile gloves
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	**Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are "free" or "natural" **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics **Sunscreen and insect repellant -** Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion

What about Closed Sites or Historic Sites?

Brownfields and other redevelopment sites

Closed military bases

Site reopener clauses in enforcement settlements

- When new information is discovered, EPA can compel settling parties to undertake additional response actions beyond previously agreed to measures
- Regulators need evidence of a known or suspected historical release, reopening can’t be just a fishing expedition
- EPA may be reluctant to open closed sites unless there is significant political pressure or likely/known impact to local drinking water supplies

5 year reviews

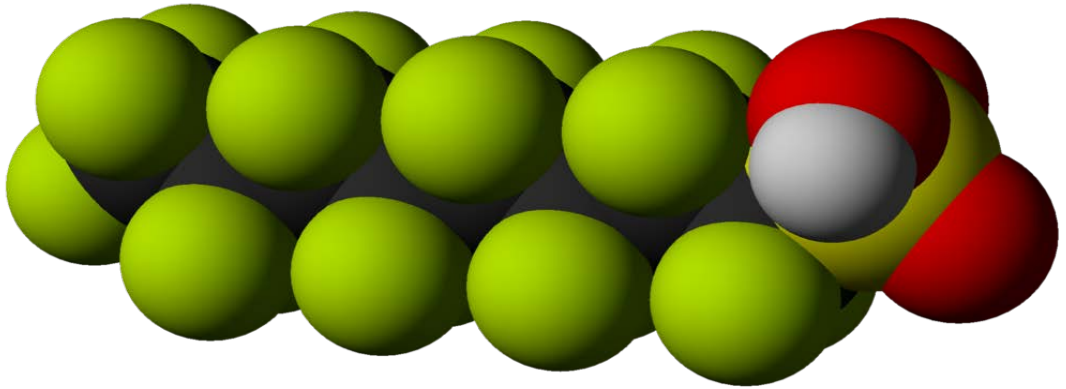
- Done at sites with waste left in place
- Primary focus is on whether remedy is working as intended for original COCs
- However, remedy may not be sufficiently protective if elevated levels of PFAS are found

Remediation challenges – PFAS

Extremely recalcitrant to degradation or destruction

Technologies under investigation for water remediation:

- Sorption - Activated Carbon or RemBind®
- Ion exchange
- Flocculation - PerfluorAd®
- Biological treatment - Pseudomonas aeruginosa strain HJ4



Contaminated infrastructure

- Can be a (or the) most significant source of PFAS flux
- Concrete in particular is a PFAS sponge and slow release media
- Drains and concrete pads are of greatest concern
  - Possible source of long term contamination due to slow leaching
- Limited feasible options for dealing with PFAS contaminated infrastructure

CONCLUSION: ***the clean-up process must also deal with contaminated infrastructure, particularly concrete***

Remediation challenges – PFAS

Field Demonstrated Treatment Technologies for Liquids

- Extraction and sorption with granular activated carbon or anion exchange resin
- Extraction and membrane filtration/reverse osmosis
- Extraction and precipitation/flocculation

Field-Demonstrated Treatment Technologies for PFAS in Solids

- Excavation and off-site landfilling or incineration
- Sorption/stabilization through ex situ soil mixing
- Ex situ thermal desorption and off-gas destruction

SOURCE: ITRC's Remediation Technologies and Methods for PFAS – Fact Sheet

Biodegradation

- Very limited research to date showing biodegradation of Per-PFAS
- Evidence of transformations of Poly-PFAS
- Ability to treat to the proposed standards?

Oxidative / Reductive Technologies

- Requires high energy and/or diverse reactive species – complex chemistry
- Several bench studies and few pilots performed showing destruction of PFAS
- Research is ongoing to treat precursors

SOURCE: XDD Environmental – PFAS Remediation Webinar – Part 1