Trihydro

WHY SHOULD WE BE CONCERNED ABOUT PFAS AND OTHER EMERGING CONTAMINANTS?

ROCKY MOUNTAIN EHS PEER GROUP

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Mitchell Olson, PhD, PE, Trihydro, Fort Collins, CO molson@trihydro.com

Emerging Contaminants

Emerging contaminants are chemicals that have been detected in global drinking water supplies at trace levels and for which the risk to human health is not yet known.

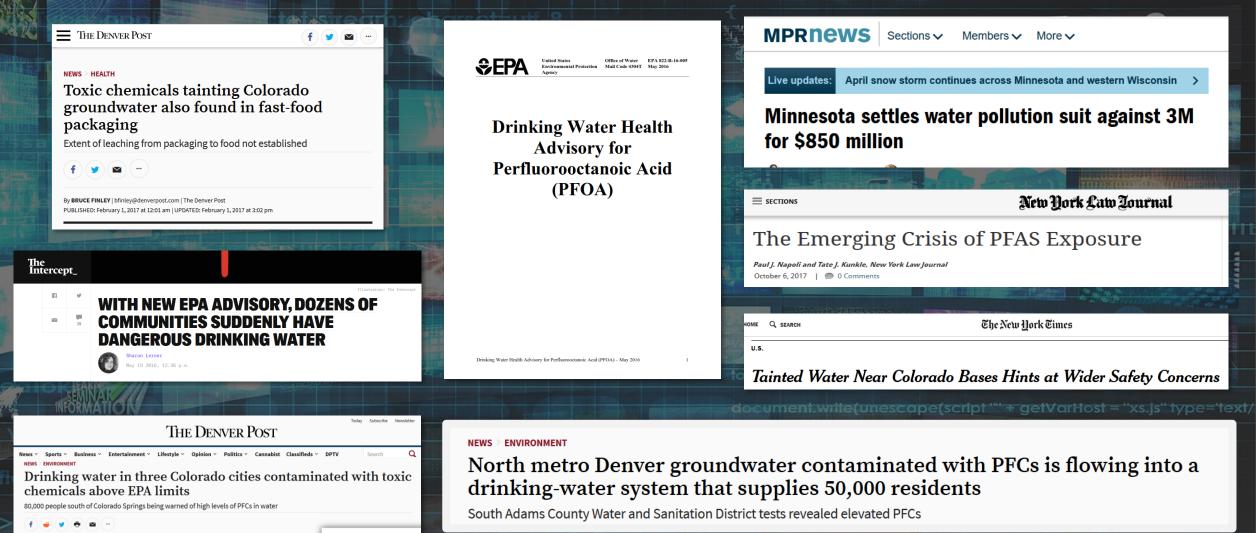
- Past emerging contaminants
 - PCBs
 - Asbestos
 - MTBE
- "Emerging" emerging contaminants
 - Pharmaceuticals, personal care products, pesticides, herbicides and endocrine disrupting compounds
 - 1,4 dioxane



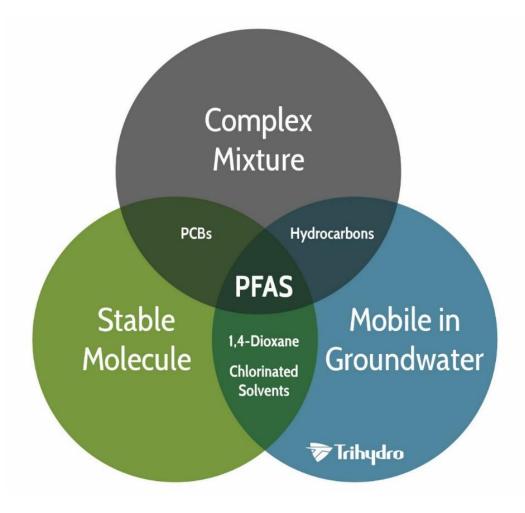


PFAS: Per- (and Poly-) Fluoro Alkyl Substances **PFCs:** Per- (and Poly-) Fluorinated Compounds (also **PerFluoroCarbons**) eponing(EALLAENOTICE)

Why Do We Care About PFAS?



Why Do We Care About PFAS?



Site Characterization

- Presence in common sampling materials (Teflon...)
- Low levels of interest (70 ppt)
- Complex mixture (3000+ compounds)
- Remediation
 - Transformable, not degradable
 - Complex sorption (polar/non-polar)
- Fate and Transport
 - High solubility
 - Non-volatile
 - Atmospheric transport on regional/global scales
 - Persistence

Perfluorinated chemical uses

- PFAS Containing Materials
- Consumer products
 - Stain/water resistant fabrics
 - Personal care products
 - Grease resistant food packaging
- Industrial applications
 - Mist suppressants
 - Aerospace
 - Electronics
- Aqueous Film Forming Foam (AFFF)



• **AFFF:** Aqueous Film-Forming Foams

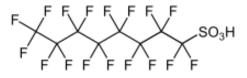
- Precursor: A polyfluorinated compound that can biotransform into a perfluorinated compound
- Short Chain vs Long Chain
 - Long chain \geq C6 for PFSAs (e.g., PFOS),
 - \geq C8 for PFCAs (e.g., PFOA)



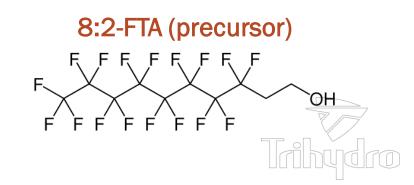


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Perfluorooctane sulfonate (PFOS)

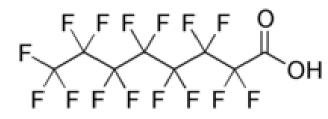


Perfluorooctanoic acid (PFOA) F F F F F F F O F F F F F F F OOH

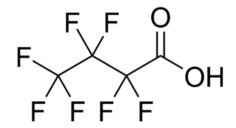


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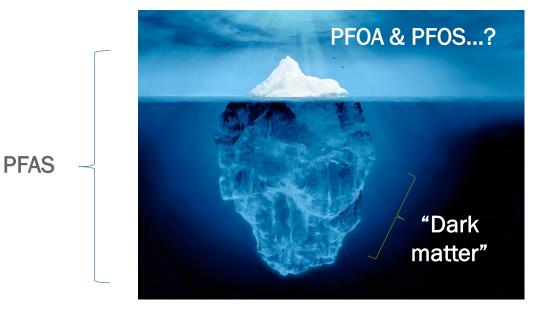


Perfluorobutanoic acid (PFBA)





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Why are PFAS so stable?





F-



Cl-

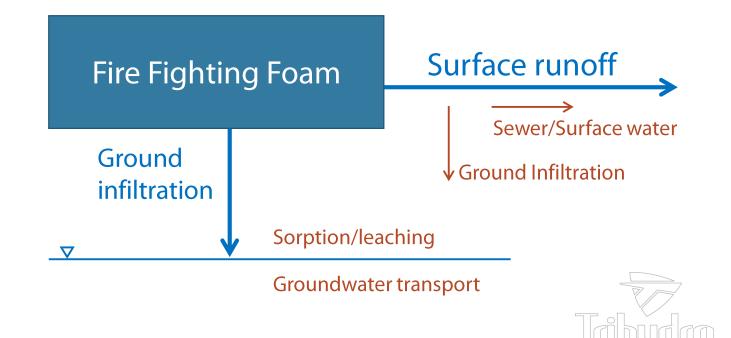




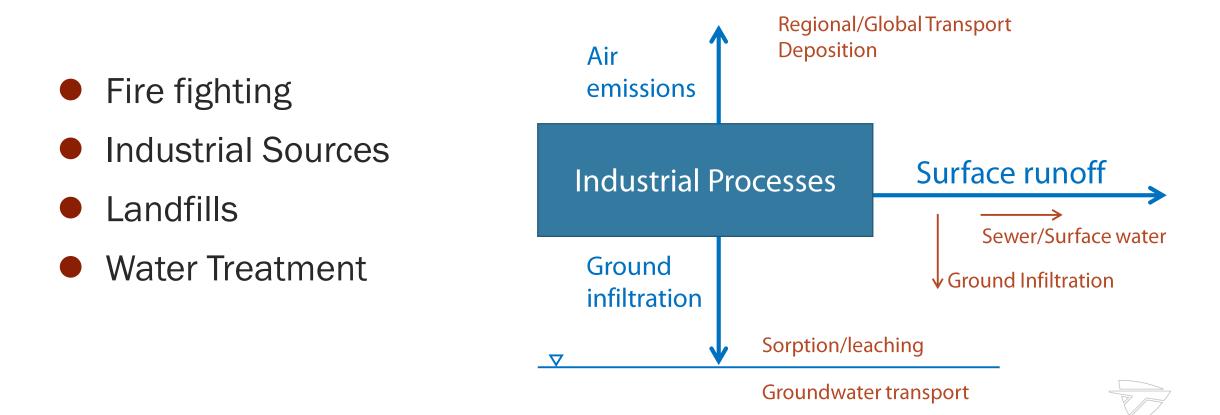
Environmental PFAS Sources

• Fire fighting

- Industrial Sources
- Landfills
- Water Treatment



Environmental PFAS Sources



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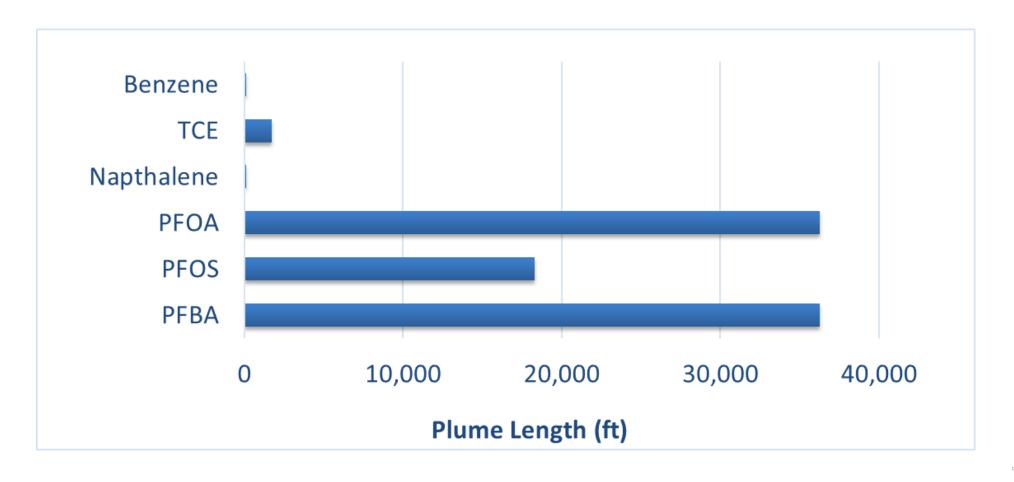
PFAS Fate and Transport

Key Considerations of PFAS in the Environment

Mobility

- High solubility
- Sorption is complex (polar/non-polar)
- PFAS compound of concern (PFOA, PFOS) are **non-volatile**
- Atmospheric transport occurs on regional/global scales
- Biotransformation
 - Bioaccumulative
 - Precursor compounds may biotransform to PFOA, PFOS
 - PFAS, as a whole, are not biodegradable

Groundwater Plume Length





Site Characterization PFAS Considerations

- PFAS-specific requirements for sampling and analysis (no Teflon!)
- QA/QC is very important for PFAS
- What PFAS to include in analysis?
 - Short list: 6 compounds on UCMR3 list
 - EPA 537: 14 compounds
 - Typical methods offer 25+ compounds
 - "Total PFAS" methods
 - TOP Assay
 - Total Organofluorine...Particle Induced Gamma Emissions (PIGE)

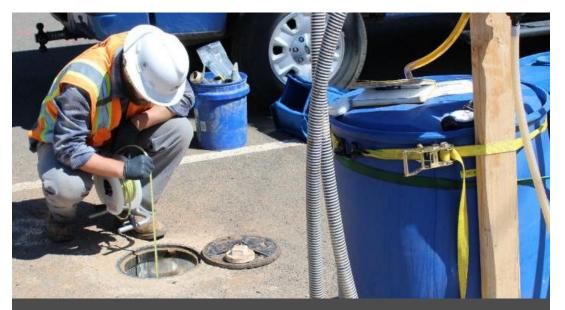


"Total" PFAS method: Total Oxidizable Precursor (TOP) assay

- Duplicate samples collected
- One is oxidized, converting many precursors to PFAAs on EPA 537 list
- Both are analyzed via EPA 537

Remediation PFAS Considerations

- Considerations
 - Degradation challenge
 - Large number of individual compounds
- In situ PFAS degradation is (currently) not feasible
- Groundwater extraction/point of use treatment is typical (currently...)
 - GAC, ion exchange (consider long- vs. short-chain PFAS)
 - Reverse osmosis, nanofiltration

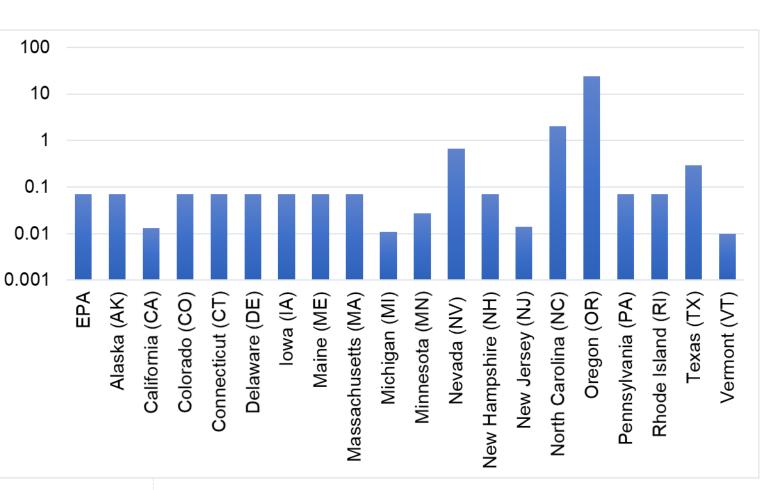


PFAS Remediation Considerations

- Resistant to air stripping & degradation
- Some PFAS partially degradable, PFAS as a whole are not
- Treatment of concentrated waste streams

PFAS: Regulatory Status

- EPA Health Advisory (HA) Levels
 - [PFOA] + [PFOS] = 70 parts per trillion (ppt)
- No EPA reg's on short-chain PFASs or precursors
- 19 state-specific MCLs or Groundwater Quality Standards
 - ITRC table (updated quarterly)



PFAS: Regulatory Status

Colorado Dept of Public Health and Environment (CDPHE)

State of Colorado

- Has adopted the US EPA's (non enforceable) HA level of 70 ppt
- Groundwater Quality Standard of 70 ppt adopted for El Paso County only
- CDPHE has committed to conducting statewide assessment of potential PFAS sources (mentioned this in EPA public forum in Colorado Springs, 8/7-8/8)
 - "CDPHE's current priority is understanding the potential impacts on drinking water sources from PFC releases. Once we have a better understanding of the potential extent of any contamination, we will evaluate the need for any statewide groundwater standards."



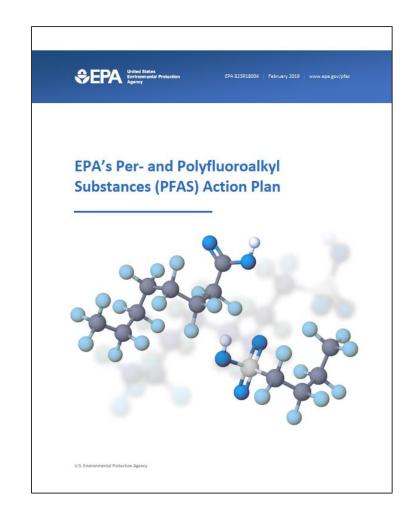
EPA Activities

EPA PFAS Action Plan released February 2019

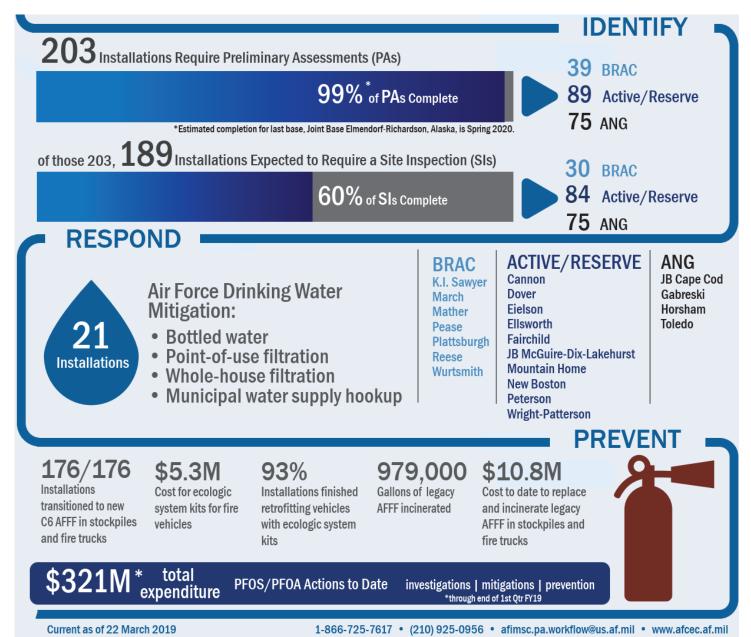
- Drinking water MCL (review 2019)
- 'Hazardous substance' designation Under CERCLA (started 2018)
- Toxics release inventory (start 2019)
- Drinking water monitoring (2020)
 Public water supply sampling under UCMR
- Research (ongoing)

Analysis, remediation, toxicity

- Enforcement (ongoing)
- Risk communication (2019)



PFAS at Air Force Facilities





The Future of AFFF



"The environmentally-mindful CHEMGUARD C606-MS Concentrate formulation contains short-chain, C-6 fluorochemicals manufactured using a telomer-based process. The telomer process produces no PFOS, and these C-6 materials do not breakdown to yield PFOA. The fluorochemicals used in the concentrate meet the goals of the U.S. Environmental Protection Agency 2010/15 PFOA Stewardship Program."



"Claims by industry that the shorter chain-length compounds are less toxic should not be accepted just because it is a convenient way to allow them to easily replace the problematic products. After all, the shorter-chain compounds are more mobile in groundwater and are nearly impossible to remove during drinking water treatment," Sedlak, 2016, Environmental Science & Technology, Fool me Once



http://www.chemguard.com/fire-suppression/catalog/foam-concentrates/aqueous-film-forming-foam-afff/C606-MS.aspx

Guidance Documents

Interstate Technology Regulatory Council (ITRC)

- **1.** Naming Conventions and Physical and Chemical Properties
- 2. Regulations, Guidance, and Advisories
- 3. History and Use
- 4. Environmental Fate and Transport
- 5. Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods
- 6. Remediation Technologies and Methods
- 7. Aqueous Film Forming Foam





https://pfas-1.itrcweb.org/fact-sheets/

Why do we care about PFAS?

PFAS compounds are "ideal" contaminants

- The issue is bigger than just PFOA and PFOS
- Complex mixture and unique chemistry
- <u>Extremely</u> low groundwater concentrations of interest (ppt)
- Ongoing challenges
 - Regulatory uncertainty
 - Uncertain/developing understanding of toxicology
 - Analysis is highly specialized
 - Remediation options exist, but are currently limited



Emerging Contaminants – 1,4-Dioxane

Presence in Environment

- Found in groundwater sites throughout US
- Used in paint strippers, dyes, greases, varnishes and waxes
- Manufacture of polyethylene terephthalate (PET) plastic
- Purifying agent in pharmaceuticals
- By-product in personal care products, shampoos, cosmetics
- Mostly associated with chlorinated solvents
 - 90% of production in 1970s
 - Stabilizer for 111-TCA





Toxicology Considerations

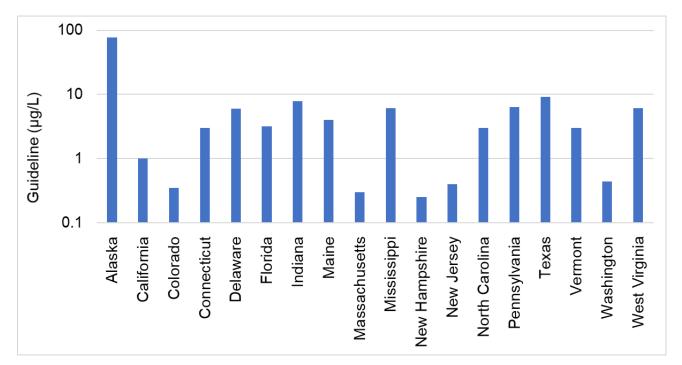
Exposure

- Ingestion of contaminated food and water, or dermal contact
- Worker exposures via inhalation of vapors
- Health impacts
 - Classified by EPA as "likely to be carcinogenic to humans"
 - Short-term exposure may cause eye, nose and throat irritation
 - Exposure to high may result in nausea, drowsiness, headache, and irritation of the eyes, nose and throat
 - Long-term exposure may cause kidney and liver damage
- Does not bioaccumulate, biomagnify, or bioconcentrate in the food chain



1,4-Dioxane Regulatory Standards for Groundwater

- No Federal Maximum Contaminant Level; Health Advisory - 0.35 µg/L
- USEPA Regional Screening Level 0.46 µg/L
- State Standards First proposed by Colorado in 2005 at 6.1 µg/L; since lowered to 0.35 µg/L (CDPHE 2012)



Variability > 2 orders of magnitude Range: 0.25 μ g/L (New Hampshire) to 77 μ g/L (Alaska)



Remediation Options

Ex-Situ

- Air stripping
- Granular activated carbon (GAC)
- Synthetic resins
- Advanced oxidation
- Aerobic bioreactor
- Other (e.g., electrolytic)

In-Situ

Physical

- Air sparging / SVE
- Thermal ?
- Chemical
 - ISCO
 - Chemical reduction (ISCR)
- Biological
 - Aerobic biostimulation
 - Anaerobic biostimulation
 - Co-metabolic processes
- Monitored Natural Attenuation



So...why do we care about 1,4-dioxane?

- Widespread occurrence in drinking water
- Very high affinity for water: high mobility, difficult removal
- **Remediation challenges:** is degradable (or extractable) under certain conditions
- **Regulatory uncertainty:** typical for emerging contaminants
- Toxicology unknowns
- What's in store...
 - ITRC team developing for 2019-2020
 - ESTCP/SERDP funded project (Extreme SVE, mixed contaminants, electrolytic)



