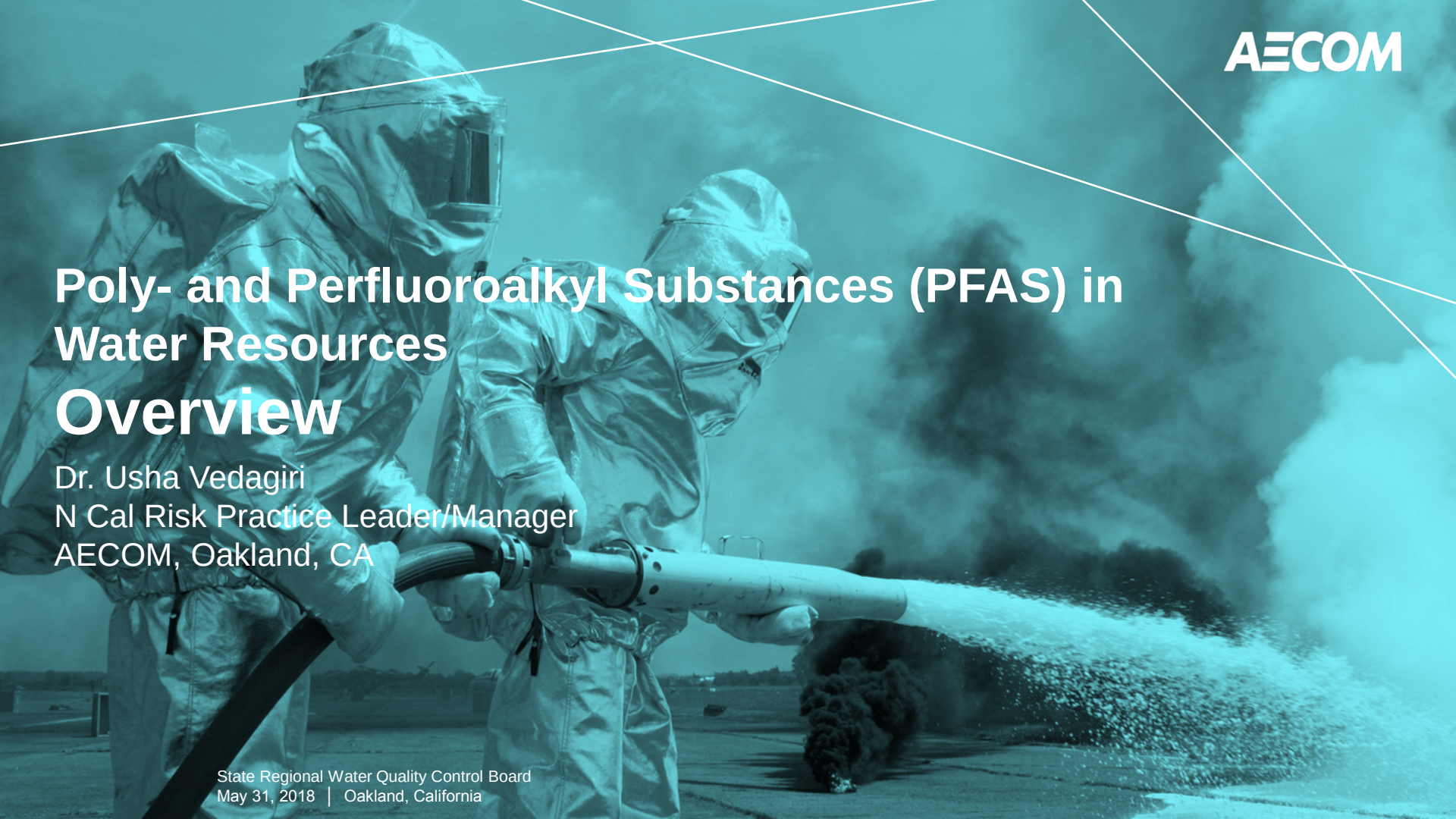

Poly- and Perfluoroalkyl Substances (PFAS) in Water Resources

Overview

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State Regional Water Quality Control Board
May 31, 2018 | Oakland, California

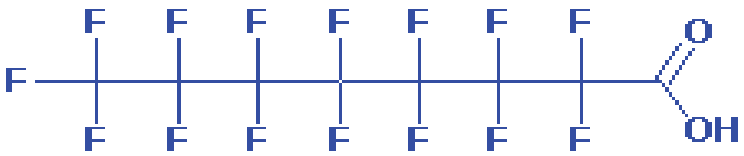
PFAS – Why Do We Care?

* Because they are everywhere and there is concern about health effects

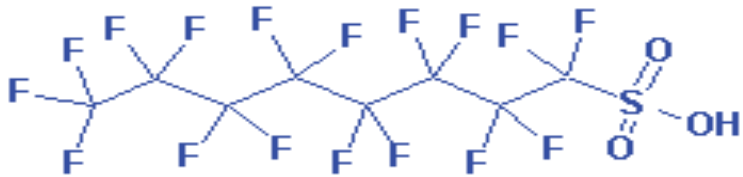
PFAS – What are they?

- Class of more than 3000 synthetic compounds formed from **carbon** chains of various lengths with **fluorine** attached to these chains (C2 to C12)
- Numerous industrial and consumer uses because they repel both water and grease
- **Stable**, **soluble**, **non-volatile**, **mobile** and **bioaccumulative**; some have identified health effects (longer chain lengths are more toxic)
- Carboxylate, Sulfonate, precursors, long-chain, short-chain…

Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonic acid (PFOS)

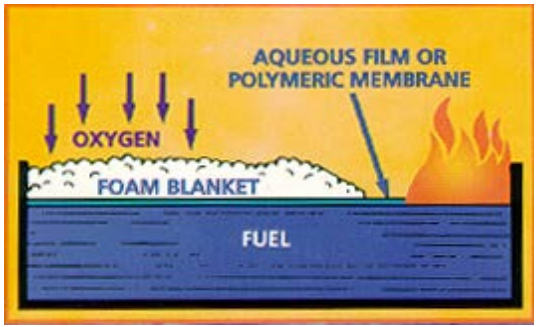


PFOS and PFOA Properties

Chemical Properties	PCB (Aroclor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	**414.07**	**538**	131.5	78.11
Solubility	0.0027 mg/L @24°C	**3400–9500 mg/L @25°C**	**519 mg/L @20°C**	1100 mg/L @ 20°C	1780 mg/L @20°C
Vapor Pressure (25°C)	$4.05x10^{-5}$ mmHg	**0.5-10 mmHg**	**$2.48x10^{-6}$ mmHg**	77.5 mmHg	97 mmHg
Henry's Constant	$4.6x10^{-3}$ atm-m^3/mol	**0.0908 atm-m^3/mol**	**$3.05 x10^{-6}$ atm-m^3/mol**	0.0103 atm-m^3/mol	0.0056 atm-m^3/mol
Organic Carbon Part. Coeff. (Log K_{oc})	4.8-6.8	**2.06**	**2.57**	2.42	2.15

Industrial Use – Aqueous Film Forming Foam (AFFF)

For petroleum fires, AFFFs develop a layered formation of foam (seals in the fire and extinguishes it) and water (cools the fire and prevents re-ignition).



Industrial Use - fluoropolymers, fluororepellents, fluorosurfactants

Aerospace

Apparel

Building and Construction

Chemicals and Pharmaceuticals

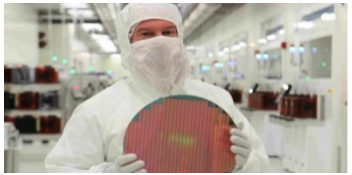
Electronics

Oil & Gas

Energy

Healthcare and Hospitals

First Responder Safety



Semiconductors

Consumer Products

Fast Food Packaging

Carpet Stain Resistant

Sleeping bag

Ski wax

And many others……

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PFAS Milestones

Date	Event
1930s	PFASs were accidentally discovered.
1940s – 1980s	Consumer products begin using PFASs (i.e. Teflon), Aqueous Film Forming Foam (AFFF) developed and used widely.
2000s	PFOS identified in biota globally (including remote regions), Stockholm POPs Convention. Some manufacturers begin replacing long-chain PFASs with short-chain PFASs.
2009	US EPA Provisional Health Advisories (400 pptr – PFOA, 200 pptr – PFOS).
2013-2015	National screening to determine if PFASs are in large scale drinking water treatment plants (US EPA - UCMR3 program).
2016	US EPA Drinking Water Lifetime Health Advisories PFOA and PFOS (70 pptr).
2017-Ongoing	Individual states developing their own groundwater/drinking water screening levels

Potential Health Effects

Human (Occupational/General Public)

- USEPA: some evidence for testicular and bladder carcinogenicity (PFOA)
- Non-cancer effects (numerous)
  - Decreased birth weight and organ weights
  - Endocrine/thyroid effects
  - Changes in cholesterol/triglyceride levels

Ecological

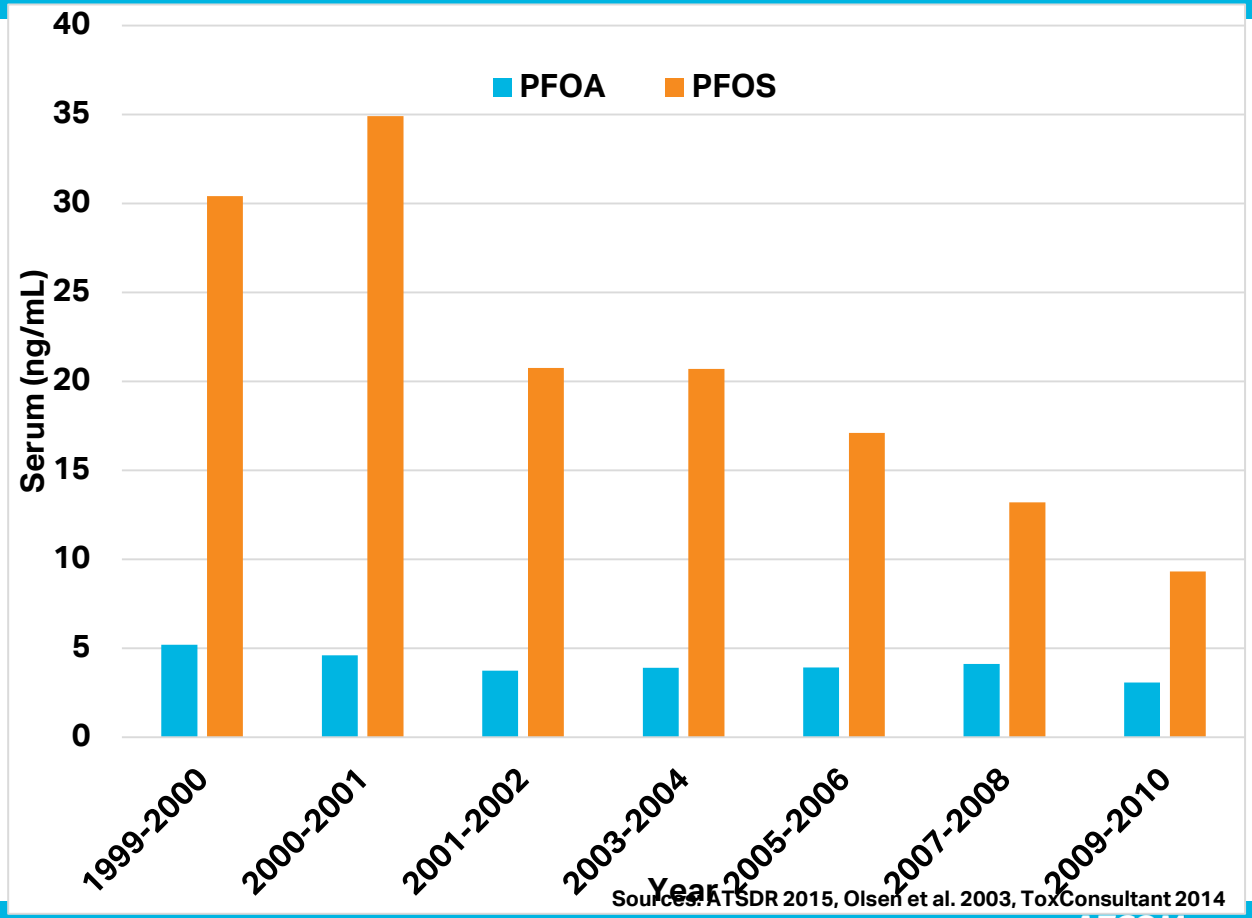
- No published EPA position
- Low to moderate acute toxicity
- Chronic toxicity at low to high doses
  - Reduced biomass/body weight
  - Changes in liver/tumors
  - Larval emergence/shell growth changes
  - Hormonal/developmental changes

PFAS Trends in Blood Serum

– Preferential binding to proteins;
  - blood serum, kidney and liver accumulation

– Decreasing Trends in PFOA in Human Blood Serum 1999-2012
  - Geometric mean: from 5.2 ug/L to 2.1 ug/L
  - 95th percentile: 11.9 ug/L to 5.7 ug/L

– **Still in production and Use in some countries**



Sources: ATSDR 2015, Olsen et al. 2003, ToxConsultant 2014

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PFAS
Regulatory Status

* Chaotic and dynamic

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Current Regulatory Status – USEPA

- Reduction in Use
  - TSCA, Clean Air Act
- USEPA PFAS Summit (May 2018)
  - Will decide on MCLs, GW cleanup standards, Hazardous Substance Designation, CERCLA
- Safe Drinking Water Act (SDWA)
  - Unregulated Contaminant Monitoring Rule 3 (2012)
  - Lifetime Drinking Water Health Advisories (2016)
  - **0.07 µg/L (70 ppt)**
- Superfund Program (CERCLA)
  - Screening levels for soil, tapwater, soil leaching to groundwater (PFBS, PFOA/PFOS)

Stockholm Convention on persistent organic pollutants (POPs)

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Current Regulatory Status – California/ Other States

- Safer Consumer Products Program
  - Consideration for listing (2018)
  - Carpets and rugs containing PFAS
- No state-wide requirements yet
- Included in Regional Monitoring Program
- Preliminary requests for inclusion in testing for emerging contaminants for some landfills
- Numerous other states have their own GW and Drinking Water values (AK, MI, MN, NH, NJ, TX, VT, etc.), some more stringent than EPA's 70 pptr advisory

Ambient PFAS Concentrations in the US and California

* Ubiquitous

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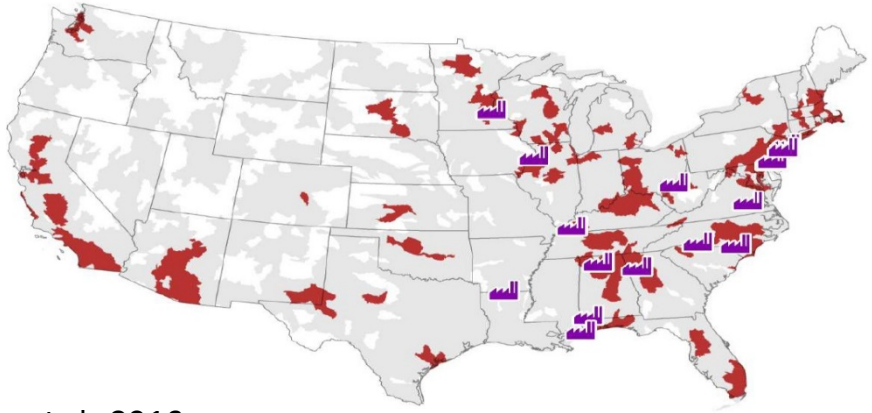
PFAS in the News

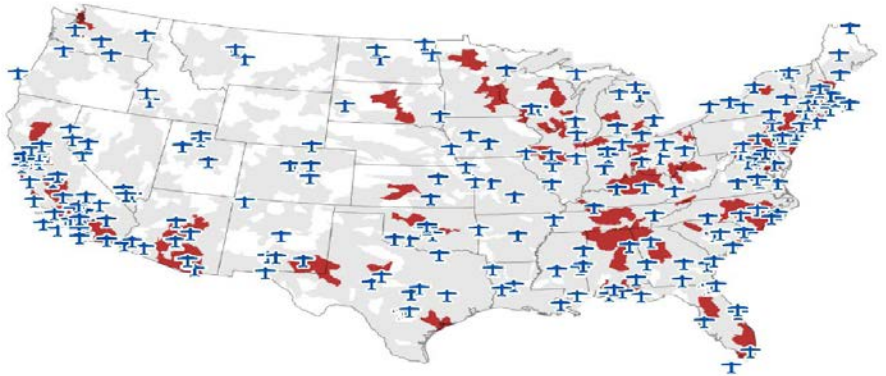
Environmental Science & Technology Letters

pubs.acs.org/journal/es

Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Area and Wastewater Treatment Plants



Hu et al., 2016



PFAS in Groundwater, Drinking Water, Surface Water

– Drinking Water (Hu et al 2016)
  - 36,149 drinking water samples from 2013-2015 UCMR data for 6 PFAS, utilities serving >10,000 people
  - Detected in 33 states, 75% of detections from 13 states including CA
  - PFOS – ND-1,800 ng/L, PFOA – ND- 349 ng/L
    - **6 million people exposed to PFAS above 70 ng/L DWHA**
  - Detection frequency of all PFAS in drinking water
    - Sourced from groundwater – 0.62%
    - Sourced from surface water – 0.31%
  - Types of PFAS
    - Sourced from groundwater – Long-chain PFAS
    - Sourced from surface water – Short-chain PFAS

Blood Serum Studies in California

- National Average (2009-2010)
  - PFOS (mean 9.3 ppb), PFOA mean (3.1 ppb) (ATSDR 2015)
  - Declining trends

- California Biomonitoring Program
  - Southern California Firefighters (Dobraca et al 2015)
    - Limited serum survey of 101 firefighters
    - Most PFAS similar to national averages except PFDeA which was higher
  - California Teachers Study (2011)
  - Maternal and Infant Study (2011)
  - Detection Frequency close to 100% (esp. PFOS and PFOA)
  - PFOS levels (means 2-12 ppb) usually higher than PFOA (means 2-4 ppb)
  - http://www.biomonitoring.ca.gov/results/chemical/154

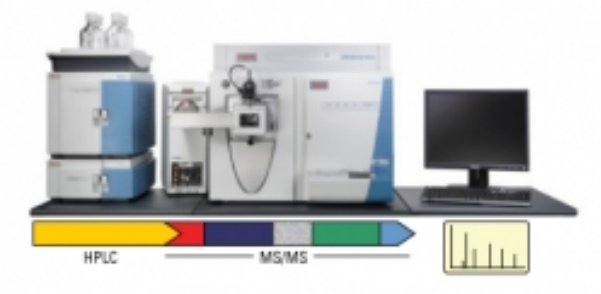
PFAS Data Quality in Sampling and Analysis

* Be very careful

PFAS Sampling

PFAS Analysis – Sampling and Analytical Methods

- Specially-trained field crew needed
- High potential for cross-contamination (restrictions on clothing and equipment)
- EPA Modified Method 537 (Liquid Chromatography - Tandem Mass Spectrometry)
- Lab SOPs are not identical
- Analysis
  - Initially PFOS and PFOA only
  - Then six PFAS from UCMR list
  - Now DoD sites do 24 PFAS
  - Can go up to 300 (Academic labs)



Human Health Risk Assessment

* Evolving

Relative Significance of Exposure Pathways

Significant

Less Significant

PFAS HHRA – Current Status

- Risk Drivers
  - Cancer and noncancer toxicity values are evolving – EPA and states
  - Drinking water screening levels are in parts per trillion range (14 – 70 ppt)
  - **Groundwater/Drinking water pathway**
  - **Non-cancer effects are the driver**
  - **Fish consumption also a concern**

- Regulatory and community framework
  - Educating the regulators and the community
  - Community blood sampling

Groundwater/Drinking Water Actions

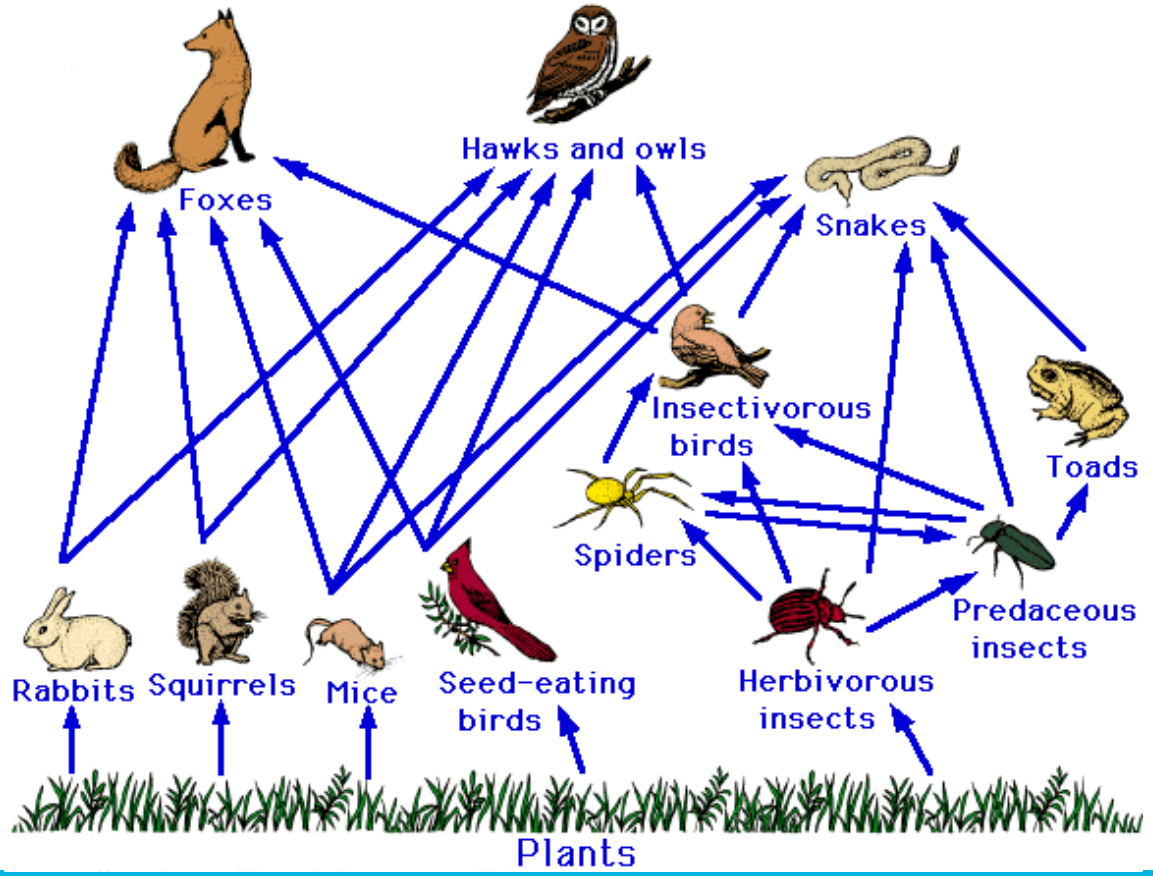
- When Health Advisories are exceeded
  - Public Water Supplies
    - Public notification requirements
    - Wells out of service
    - Blending
    - Provision of alternative water supplies
  - Contaminated Groundwater
    - Site-specific risk assessment
    - Default clean-up goals
    - Fear of liability

Ecological Risk Assessment

* Done when needed

Ecological Risk Assessment – Overview

- Multiple receptor types
- Multiple pathways
  - Direct exposure to soil, water, sediment
  - Food web exposure
- **Bioaccumulation is a key issue but no uptake models yet**



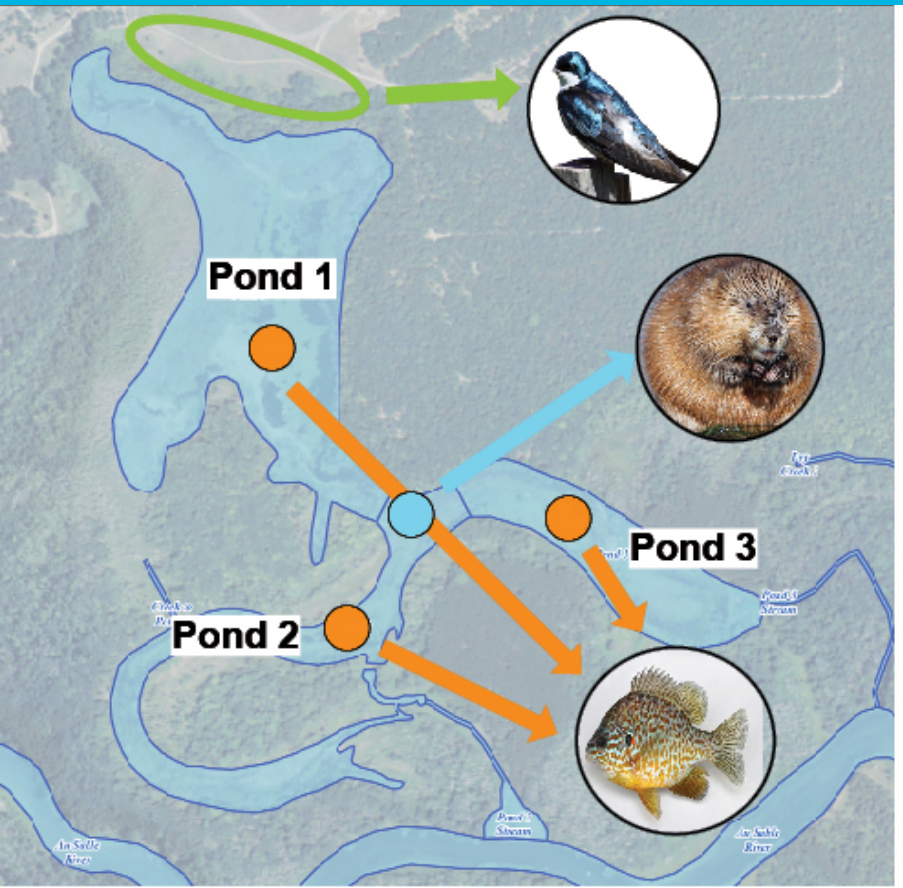
ERA – Screening and Site-Specific Evaluation

- No consensus-based screening levels, select our own site-appropriate values
- Can screen out sites with low level contamination

Medium	Screening Values	Basis
Surface Water (Aquatic Biota) (ng/L)	20 – 460,000	Direct toxicity
Surface Water (Avian Wildlife) (ng/L)	2 – 47	Food-web bioaccumulation
Fish Tissue (for predators) (mg/kg)	87	Food-web bioaccumulation

- Toxicity testing if screening levels are exceeded
  - Surface water testing with daphnids, fathead minnows, other species
  - Sediment testing with midge and amphipod tests, other species
- Bioaccumulation also needs to be considered

Site-Specific Data Collection at an Air Force Base



Muskrats

- 2 Muskrat Samples

Fish

- 43 Fish Filet Samples
- 20 Fish Liver Samples

Tree Swallows

- 20 Tree Swallows Samples
- 4 Diet Samples (Stomach Content)

Surface Water

- 12 Surface Water Samples

Sediment

- 9 Sediment Samples

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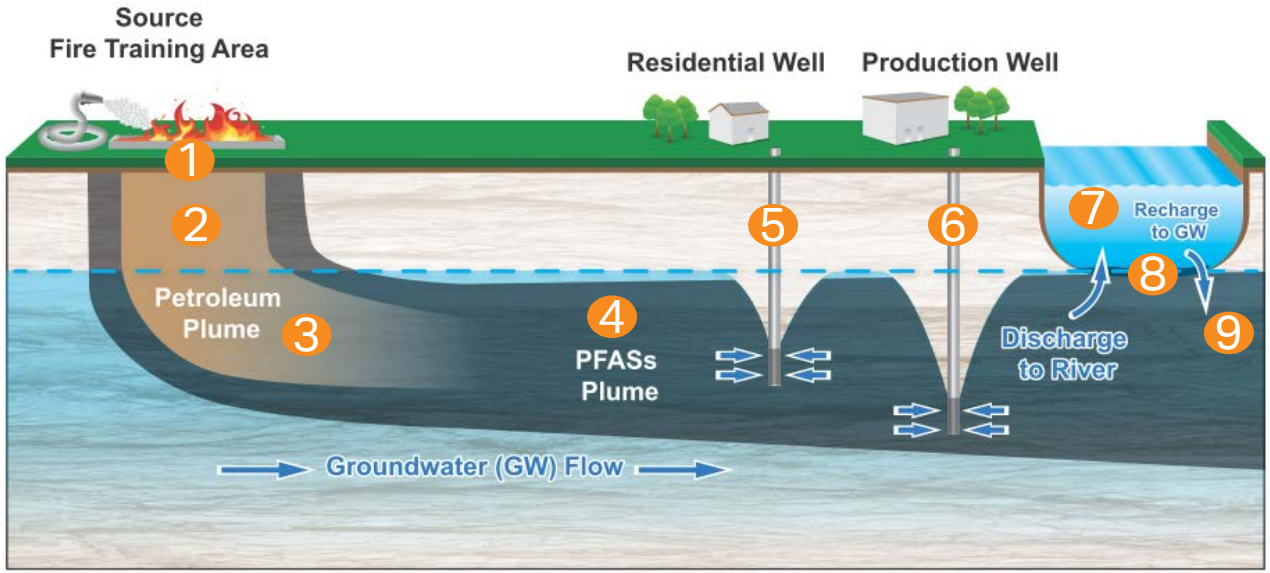
Are short-chain PFAS “better” than long-chain PFAS?

- Short-chain PFAS (<7C) replacing Long-Chain PFAS in many consumer and industrial products
  - Example Short-chain PFAS – PFBS (4C), PFBA (4C), and PFHxA (6C)
  - Are Short-Chain PFAS “better”?
  - **Many unknowns and uncertainties, much more information needed**

	Short-Chain PFAS	Long-chain PFAS
Blood Elimination half-life (mammals)	3 – 46 days	2 yrs – 9 yrs
Bioconcentration Factors (Water to Fish tissue)	<1	100’s – 1,000’s
Bioaccumulation Factors (Water+Diet to Fish tissue)	ND to Low	Bioaccumulative
Biomagnification Factors (BMF)	None noted	Do biomagnify
Toxicity (human and ecological), may depend on consideration of administered dose vs internal dose	Similar or lower (not necessarily non-toxic)	Low-moderate

Conceptual AFFF Site Model – Remediation Scenarios



1. Surface Soil
2. Subsurface Soil
3. Source Area GW
4. Downgradient GW Containment
5. Residential Well GW Treatment
6. Production Well GW Treatment
7. Surface Water
8. Sediment
9. Offsite GW Impacted by Surface Water

Shortlist of Water Treatment Technologies Studied

Ex-Situ		In-Situ
• **GAC** • Modified zeolite • **Ion exchange resin** • Reverse osmosis • Chemical or electro-coagulation • Nano membrane filtration	Separation	• PlumeStop • Phytoremediation
• Incineration • Advanced oxidation • **Electrochemical oxidation** • Sonolysis	Destruction	• Chemical oxidation • Chemical reduction • Microbial degradation • Fungal degradation • Enzyme catalyzed oxidation

What We Don’t Know about PFAS

– There are numerous data gaps and uncertainties

– To name a few
  - Thousands of unevaluated PFAS compounds
  - Analytical methods development
  - Fate and transport parameters
  - Behavior and potential toxicity of precursors
  - Potential toxicity of long-chain and short—chain PFAS beyond the most commonly-studied compounds
  - Hazard assessment, toxicokinetics, toxicity assessment methods
  - Degradation potential
  - Effectiveness of remedial technologies in the field
  - And more…

Selected Resources for PFAS in Water

Hu et al. 2016. Detection of PFAS in US Drinking Water Linked to Industrial Sites, Military Fire Training Areas and Wastewater Treatment Plants. ES&T Lett, 2016, Oct 11, 3(10) 344-350

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National Groundwater Association. 2018. Groundwater and PFAS: State of Knowledge and Practice. http://www.ngwa.org/Media-Center/news/Pages/Groundwater-and-PFAS-State-of-Knowledge.aspx

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San Francisco Estuary Institute (SFEI). PFAS in San Francisco Bay: Synthesis and Strategy. http://www.sfei.org/sites/default/files/events/Session%2004-%20A%20Sedlak%20PFAS.pdf

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Vedagiri et al. 2018. Ambient levels of PFOS and PFOA in the Multiple Environmental Media. J. Remed. 28(2):9-51 **(Contact author for updated corrected pdf)**

Questions?

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