

Per- and polyfluoroalkyl substances (PFAS) - Overview of Technical and Regulatory Issues Resulting from AFFF Use at Military and Industrial Facilities

Jason Conder, PhD

2018 SAM Fall Forum

San Diego, CA

October 30, 2018

Geosyntec 
consultants

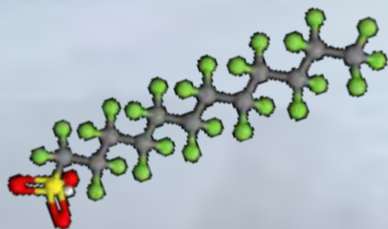
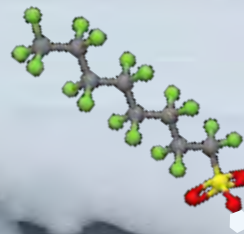
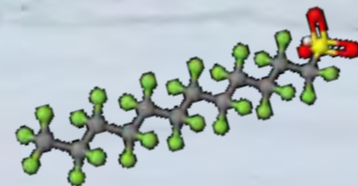
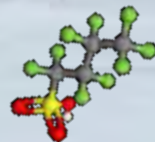
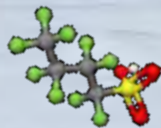


Aqueous Film Forming Foam (AFFF) Not snow!



Aqueous Film Forming Foam (AFFF) Not snow!

Perfluoroalkyl and
polyfluoroalkyl substances
(PFAS)



- PhD Environmental Toxicologist and Chemist
- PFAS site investigation and risk assessment
- Various PFAS projects since ~2005
 - 3 peer-reviewed papers on PFAS (chemistry, ecotoxicology, risk assessment)
 - US Department of Defense Frequently Asked Questions (FAQ) PFAS
 - US Department of Defense Guidance for PFAS Ecological Risk Assessment (in progress)
 - Several ongoing risk assessments for PFAS

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Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

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ABSTRACT
The primary aim of this article is to provide an overview of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the environment, wildlife, and humans, and recommend clear, specific PFASs. The overarching objective is to unify and harmonize common global scientific, regulatory, and industrial communities. A particular substance related to the long-chain perfluoroalkyl acids, and substituted perfluoroalkyl acids or their precursors. First, we define PFASs, classify

Critical Review

Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds

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Received 14 July 2010; Accepted 14 July 2011

ABSTRACT
Perfluorinated carboxylates (PFCAs), including perfluorooctanoate (PFO), perfluorononanoate (PFNA), and perfluorodecanoate (PFDA), the anions of perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA), respectively, have been detected in a variety of wildlife across the globe (1, 2). The cataloging of wildlife biological samples containing PFCA residues attests to the widespread presence of these compounds due to multiple global sources (3), with the majority of sampling being conducted to support hypotheses regarding long-range fate and transport, temporal trends, and industrial sources (4–6). The analysis of chemicals in wildlife does not necessarily imply high bioaccumulation potential for any chemical, but comprises a standard element of many environmental monitoring programs. There are many readily available samples of biological tissues that have been collected during the past 20–30 years from a variety of organisms in support of monitoring programs tracking bioaccumulative persistent organic pollutants (POPs) (7), and a network of tissue collection efforts continues to supply environmental scientists with samples. However, temporal samples of abiotic media are more difficult to obtain, exhibit concentrations of PFCAs near current method detection limits, and may be more variable than biota samples due to low analyte concentrations, sample contamination, and other quality assurance/quality control issues (8–10). The large number of biota samples collected that contain quantifiable amounts of PFCAs, the ongoing scientific discourse regarding the high persistence and long-range fate and transport of PFCAs, and perceived similarities with perfluorinated sulfonates (PFASs), including perfluorooctane sulfonate (PFOS), have prompted concerns regarding the bioaccumulation potential of PFCAs (1, 1–10). This review evaluates concerns regarding the bioaccumulation potential of PFCAs in the existing regulatory and scientific context used to qualify the bioaccumulation potential of other persistent organic chemicals.

Introduction
With the ongoing investigations of Perfluoroalkyl and

Modeling avian exposures to perfluoroalkyl substances in aquatic habitats impacted by historical aqueous film forming foam releases

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HIGHLIGHTS
• We modeled the exposure of 7 PFASs to biota in aquatic ecosystems impacted by AFFF.
• Modeled exposures exceeded levels of potential concern for 3 of 5 model organisms.
• Perfluoroalkyl sulfonic acids, especially PFOS, comprised >90% of PFAS exposures.
• Sediment, not water, represented the primary abiotic source of PFAS exposure.

GRAPHICAL ABSTRACT

ARTICLE INFO
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Keywords: Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS); Aqueous Film Forming Foam (AFFF); Perfluoroalkyl sulfonic acids; perfluoroalkane sulfonates (PFAS); Ecological risk assessment; Bioaccumulation

1. Introduction
With the ongoing investigations of Perfluoroalkyl and

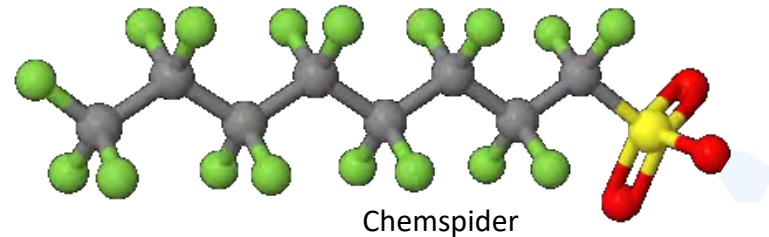
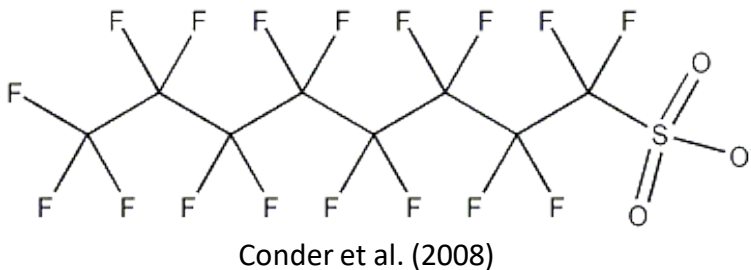
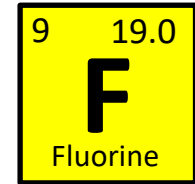


- Key issues for assessing and managing Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
 - It's not just a drinking water issue
- Topics
 - Brief review of PFAS organic chemistry, sources, and AFFF
 - PFAS fate and exposures
 - Toxicology and risk assessment
 - Regulations

PFAS Chemistry and Sources



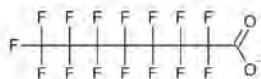
- PFAS: **P**erfluoroalkyl and **P**olyfluoroalkyl **S**ubstances
- A family of synthetic organic compounds that contain multiple fluorine (F) atoms



Perfluorooctane sulfonate (PFOS)

- **Incorrectly referred to as “PFCs”**
 - Greenhouse gases regulated by the Kyoto Protocol
 - PFCs are one of the families of PFAS (all PFCs are PFAS, not all PFAS are PFCs)

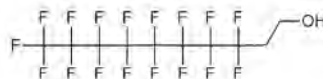
- Hundreds-thousands of compounds



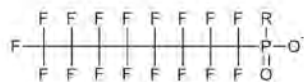
Perfluorocarboxylic acids
(ex. PFOA)



Perfluorosulfonic acids
(ex. PFOS)



Fluorotelomer alcohol
(ex. 8:2 FTOH)



Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPI)



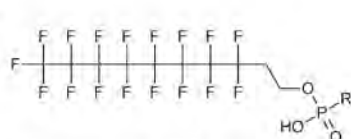
Perfluorosulfonamide
(ex. FOSA)



Perfluorinated cyclo sulfonates
(ex. PFECHS)



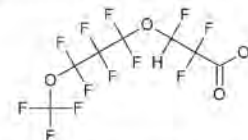
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



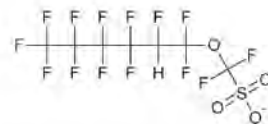
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxo-3H-perfluorononanoate)



Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

Table 1. Newly Discovered PFASs Found in AFFFs and CPs

Class Number	Structure	n ^{1,2}	Acronym ³	Confidence Level ^{1,2}	AFFF/CP Found In
1		3-6	N-SP-FASA	2b	B, C
2		3-8	N-SPAmP-FASA	2b	A, B, C, F
3		3-9	N-SHOAmP-FASA	3/	C, D, E, F, G
4		4-6	N-SPHOAmP-FASA	3	B, C
5		3-8	N-SPAmP-FASAPS	2b	A, B, C
6		5-6	N-diHOAmP-FASA	3	B, C, O
7		2-4	N-diHOAmP-FASAPS	3	A, B, C
8		2-8	N-HOEAmP-FASAPS	2b	A, B, C
9		2-8	N-HOEAmP-FASE	2b	A, B, C, D, E
10		4-6	N-HOEAmP-FASA	3	B, C

Lindstrom et al. (2011); Barzen-Hanson et al. (2017)

- Excellent surfactants
- High production volumes, variety of applications since the 1940s-1960s
 - Aqueous Film Forming Foam (AFFF)
 - metal plating (mist suppression)
 - fluoropolymer manufacture
 - polymeric/ surfactant products in leather, paper, textiles, sealants, paint, cleaning products
 - pesticides (Sulfuramid)
 - photographic applications / photolithography
 - semiconductors
 - aviation hydraulic fluids



- **AFFF = Aqueous Film Forming Foam**
 - Complex, proprietary mixtures of fluorinated and hydrocarbon surfactants, water, corrosion inhibitors, solvent
 - ~1-10% PFAS by weight
 - 10s to 1000s of liters per use
- **History**
 - Mid 1960s – 1970: 3M sole source supplier of AFFF
 - 1973: National Foam
 - 1976: Ansul
 - 1994: present: Angus, Chemguard, Fire Service Plus
- **Multiple AFFFs used at most sites, and PFAS composition varies by manufacturer**



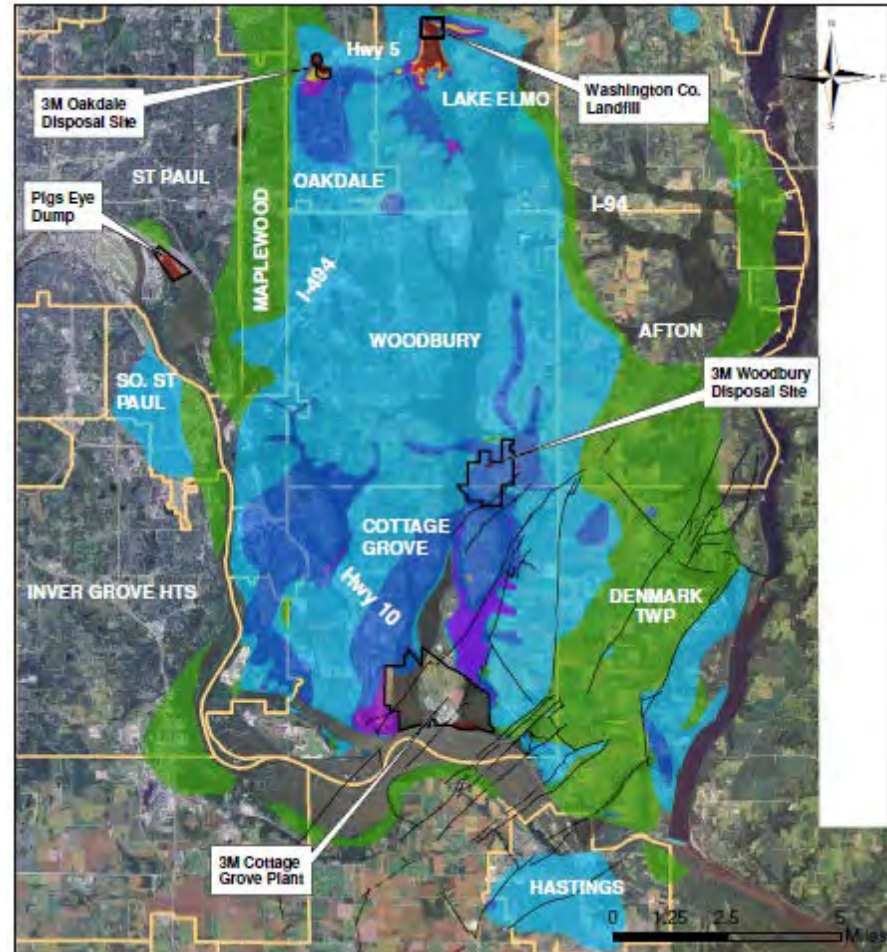
- 75% of AFFF produced was used by military
- Other AFFF users
 - Oil and gas industry
 - Bulk fuel storage
 - Chemical manufacturers
 - Airports
 - Municipalities
 - Landfills
 - Misc. (metal working industries, print industries, communities)



PFAS Fate and Exposures

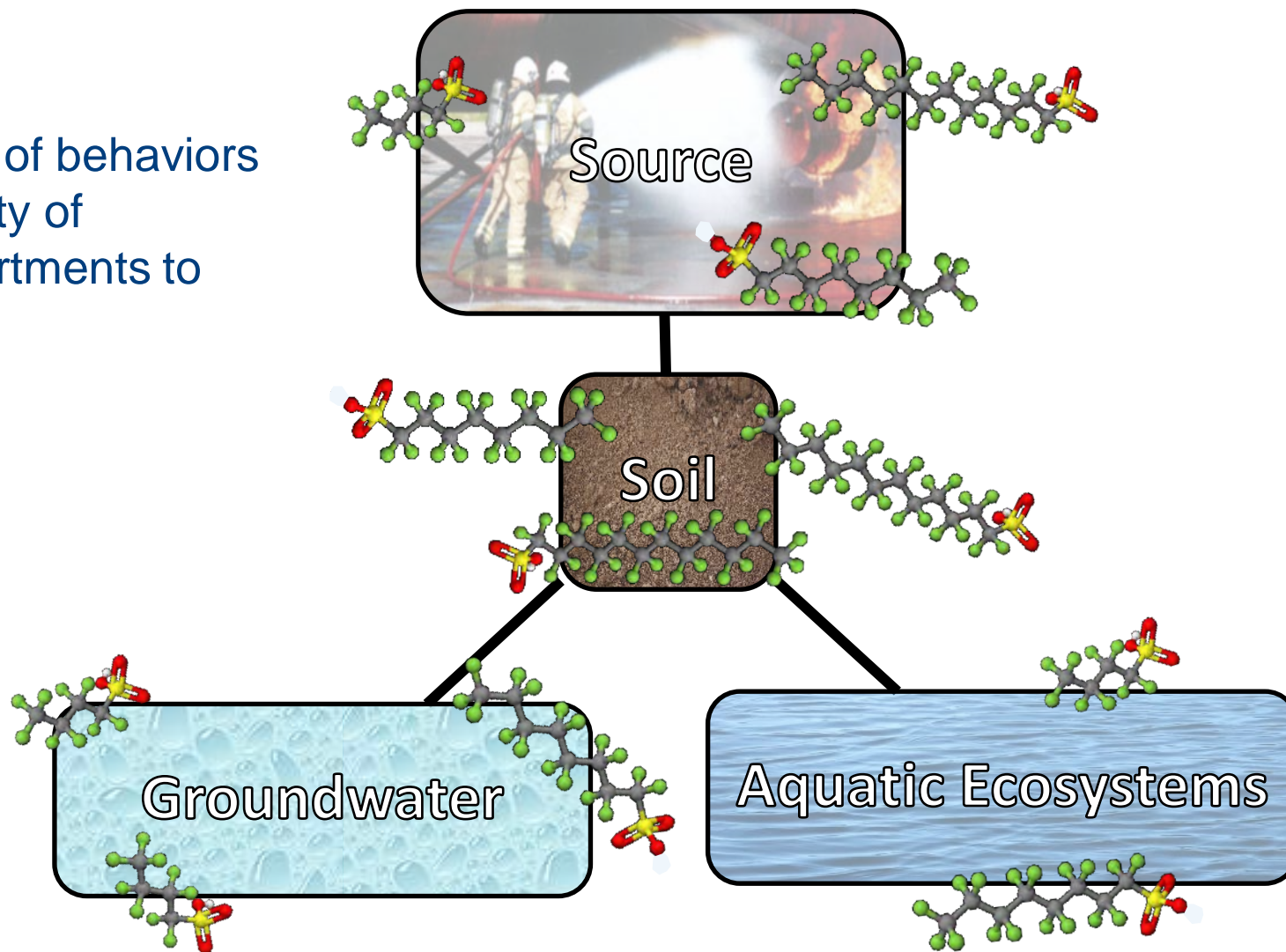


- Moderate-high water solubility/mobility
 - Groundwater plumes from contaminated areas many miles long
- Extremely persistent or transform to persistent PFAS
- Persistent PFAS at contaminated sites not volatile
- Can also partition to soils and sediment (organic matter)



Minnesota 3M PFAS plumes in groundwater 10+ miles long, cover over 100 miles² (MDH, 2012)

- Range of behaviors = variety of compartments to track



- Detectable in nearly any biological tissue
- Partitions to protein (proteinophilic), not fat/lipid
 - Blood, liver, kidney, muscle are primary repositories
 - Traditional models not useful for understanding or predicting bioaccumulation and toxicity
- Not metabolized, or metabolizes to persistent PFAS (precursors)



99% of California teachers with detectable PFAS

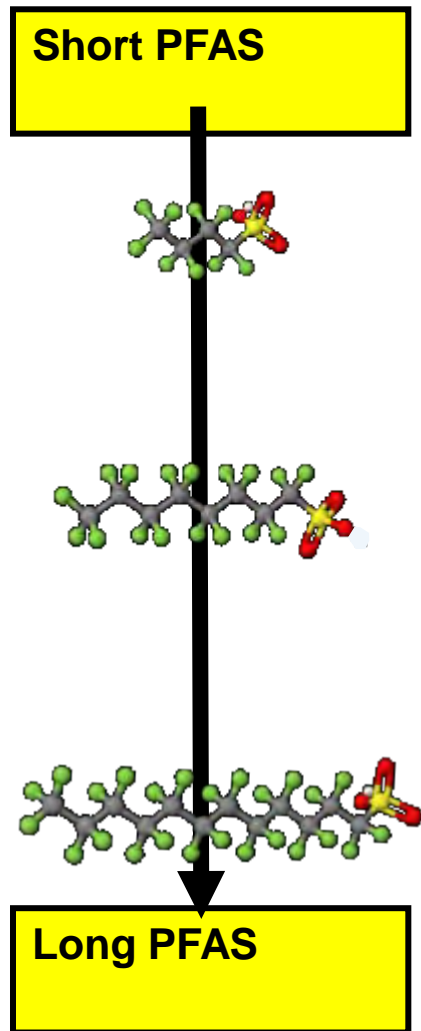
Chemical Group: Perfluorochemicals (PFCs)
> Measured in: Serum

A+

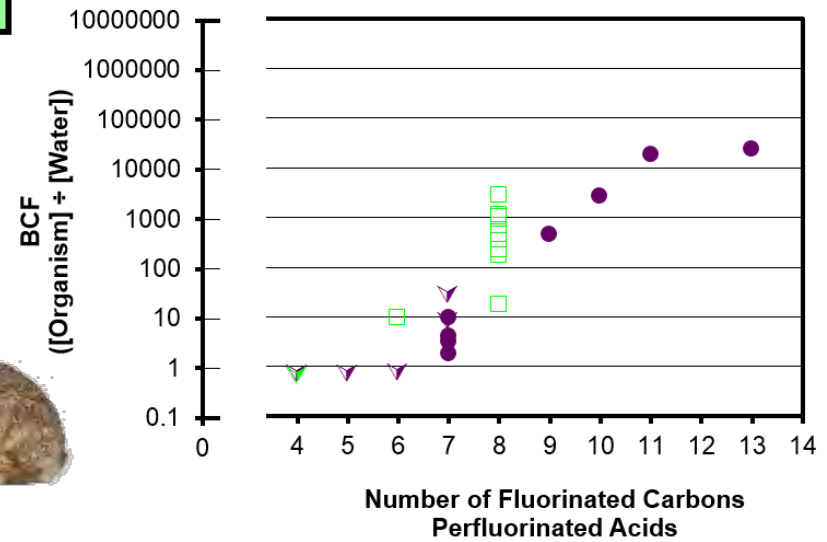
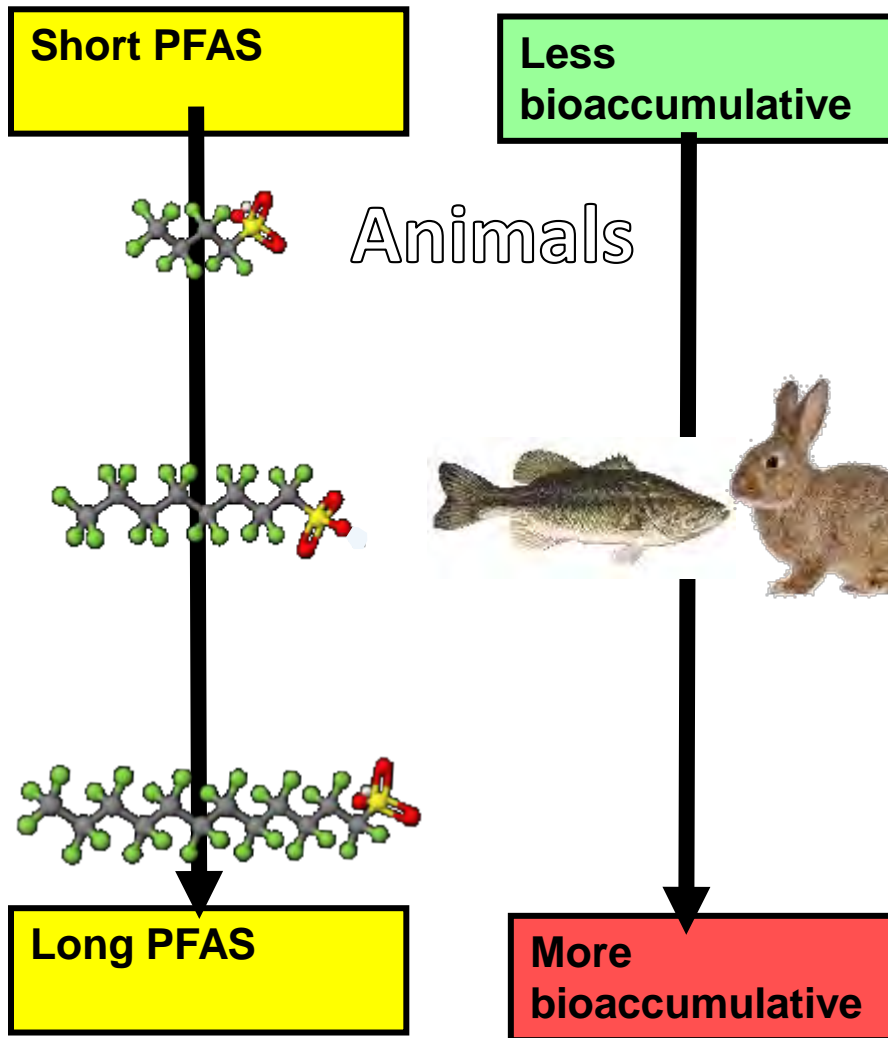
Project: California Teachers Study (CTS)
> Study Group: All
> Sample Collection Date: 2011

Source: Open source graphics from USFWS, Cal EPA DTSC

Chemical Size Affects Bioaccumulation

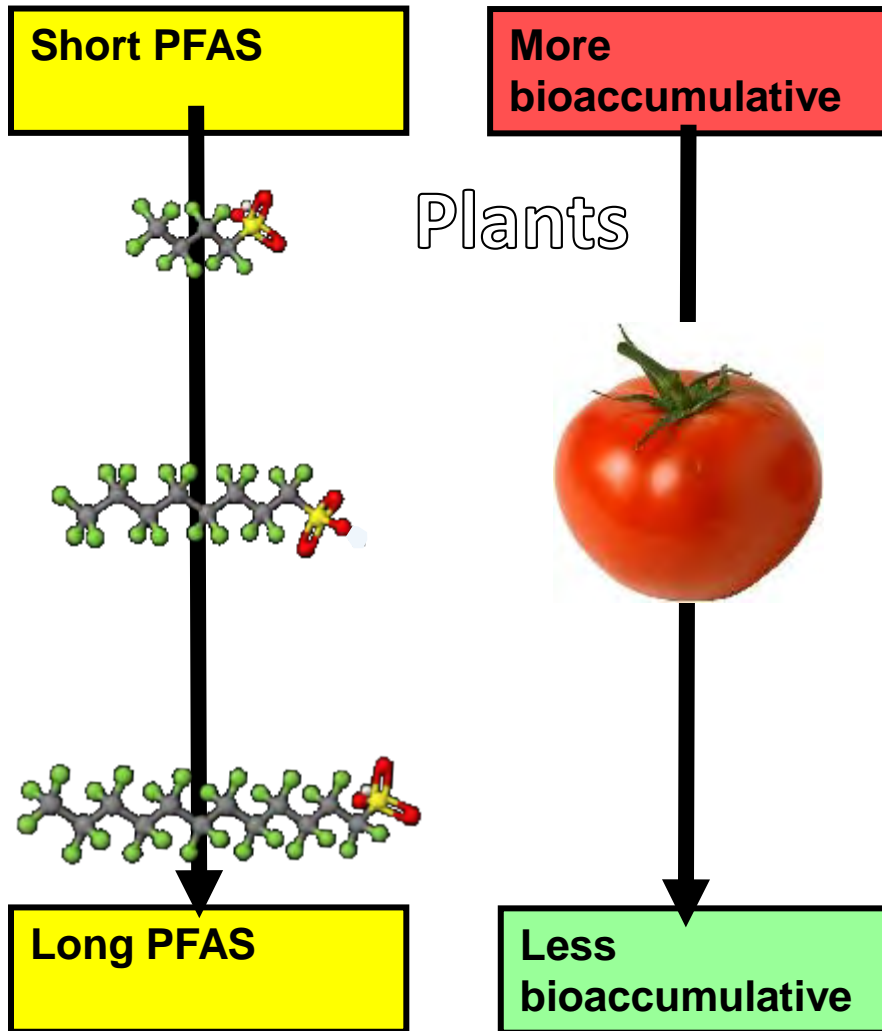


Chemical Size Affects Bioaccumulation



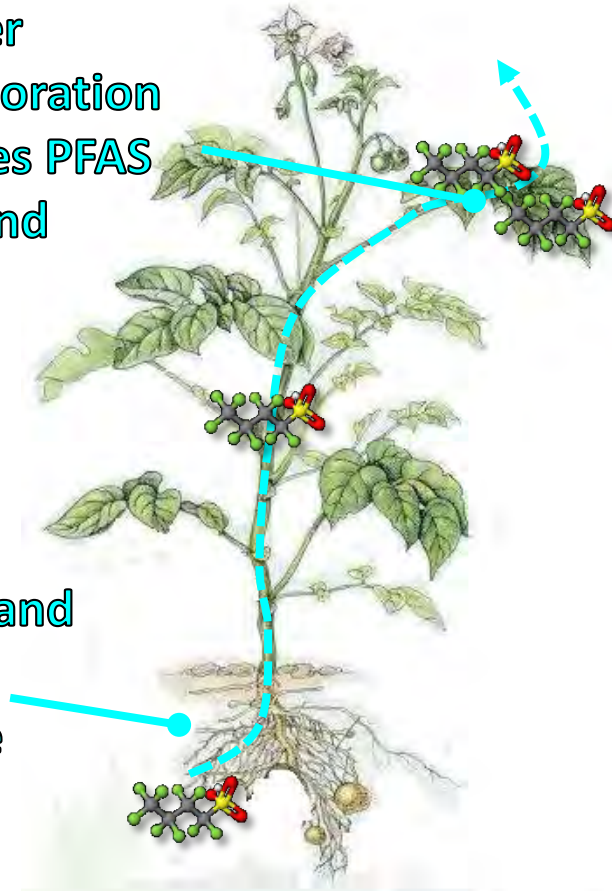
Conder et al. (2008) Environ. Sci. Technol.
42:995-1003

Chemical Size Affects Bioaccumulation



water evaporation leaves PFAS behind

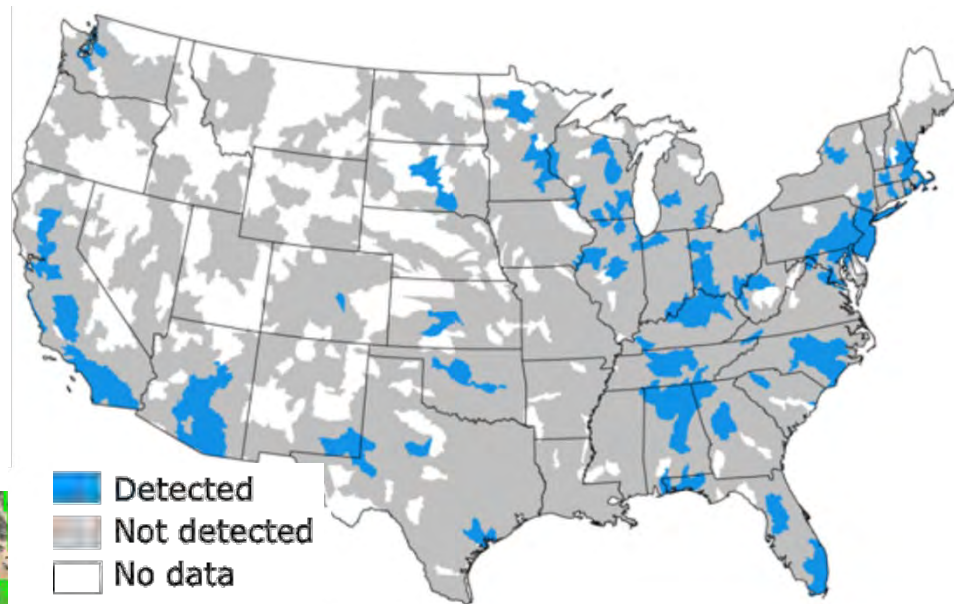
water and PFAS uptake



- Major
 - Diet (bioaccumulation)
 - Fish and seafood
 - Homegrown produce
 - Drinking water
 - Incidental soil/dust ingestion
- Usually insignificant or minor
 - Dermal absorption
 - Inhalation

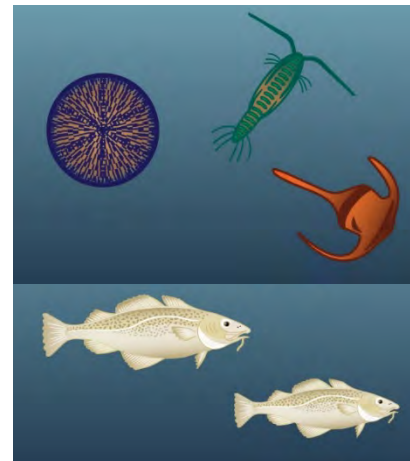
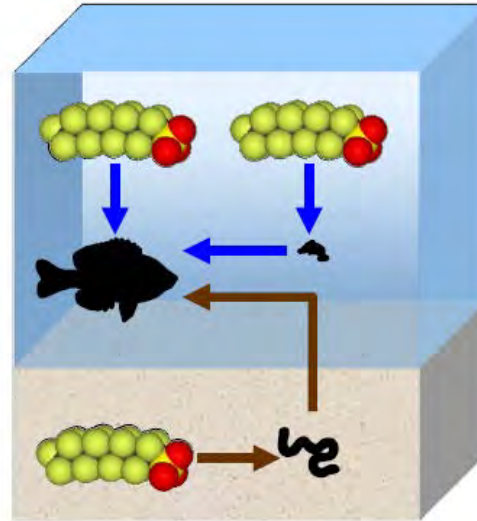


- PFAS detected above drinking water health criteria > 60 drinking water systems
 - EPA Unregulated Contaminants Monitoring program (UCMR3)

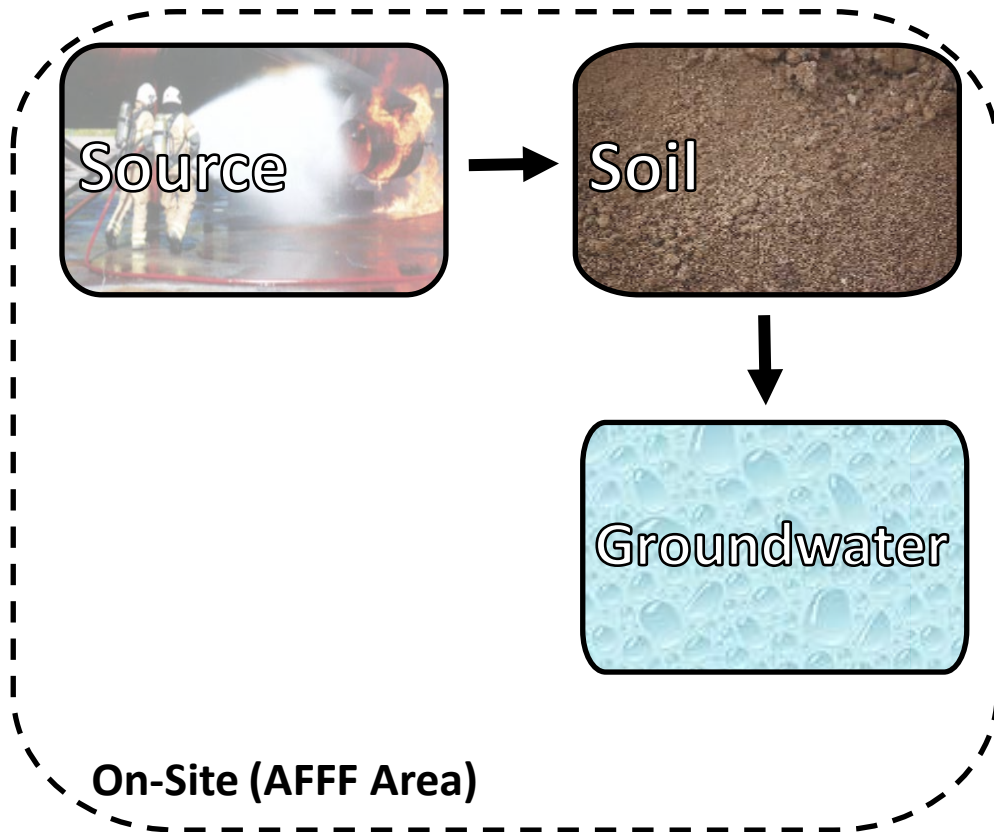


From Hu et al. 2016. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. ES&T Letters. 2016, 3 (10) pp. 344-350 (open access article). Copyright American Chemical Society.

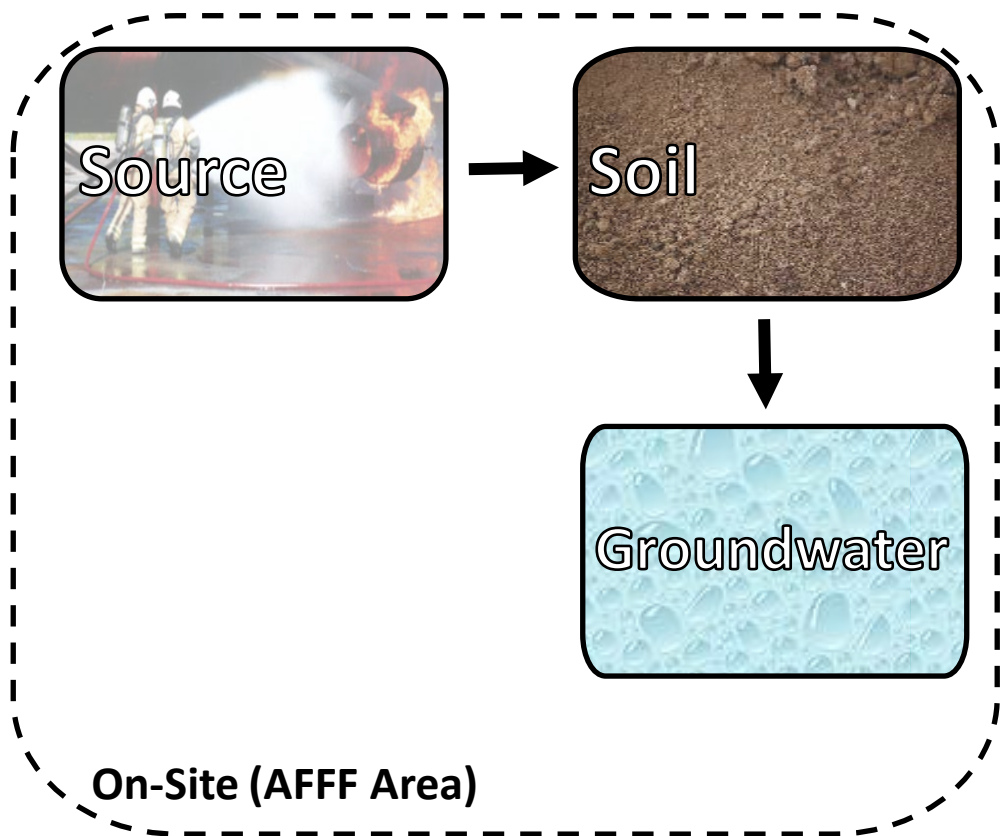
- Major
 - Incidental soil/sediment ingestion
 - Diet (biomagnification)
 - Aquatic food webs particularly susceptible to longer PFAS
 - Plants readily accumulate shorter PFAS
- Dermal absorption (aquatic life)
- Insignificant/minor
 - Inhalation



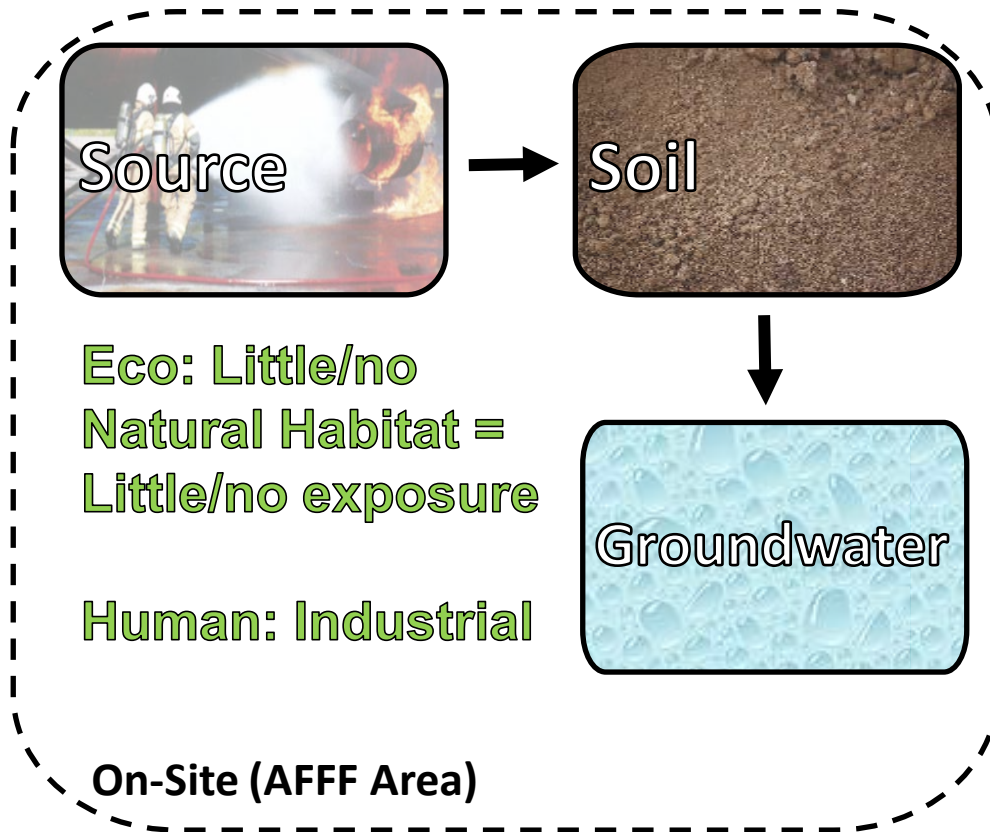
Conceptual Site Model for AFFF Risk



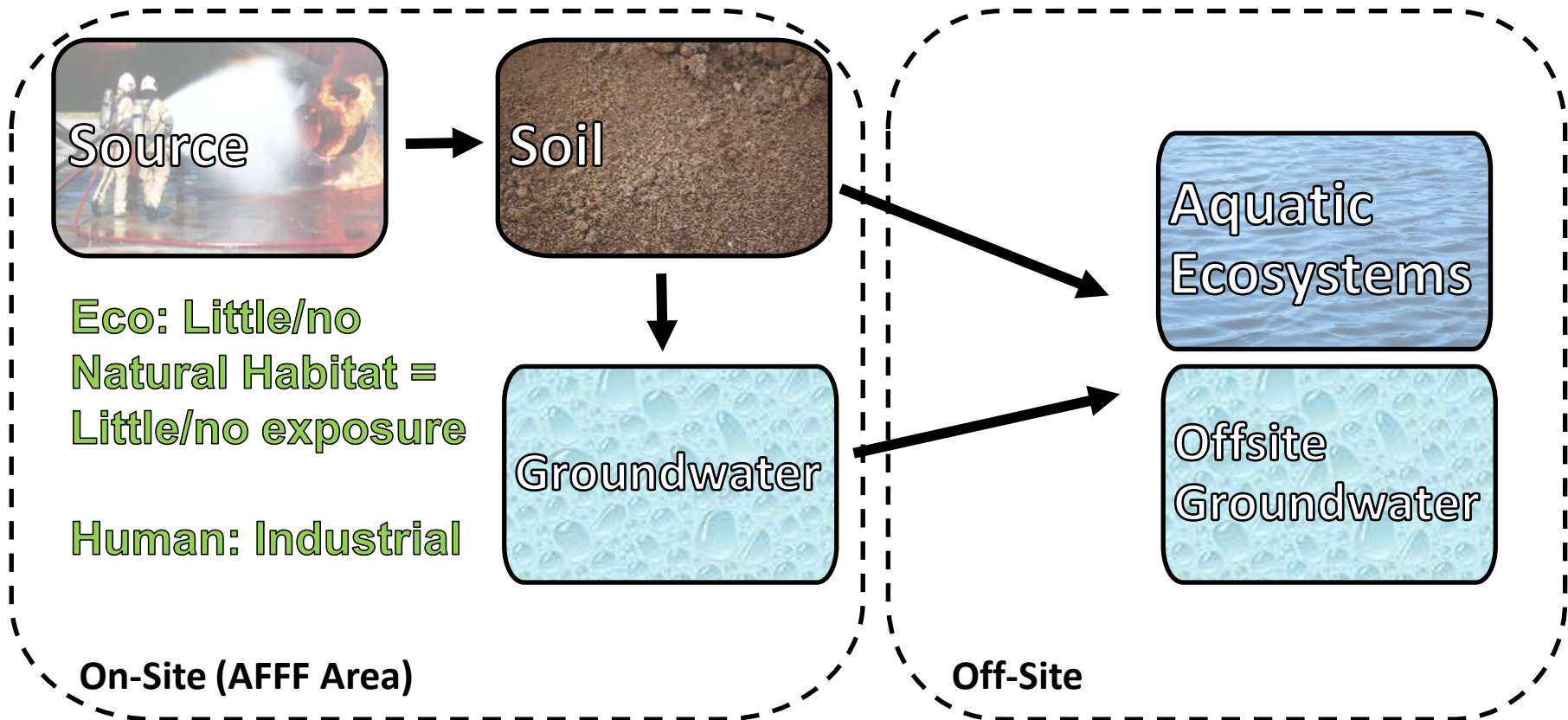
Conceptual Site Model for AFFF Risk



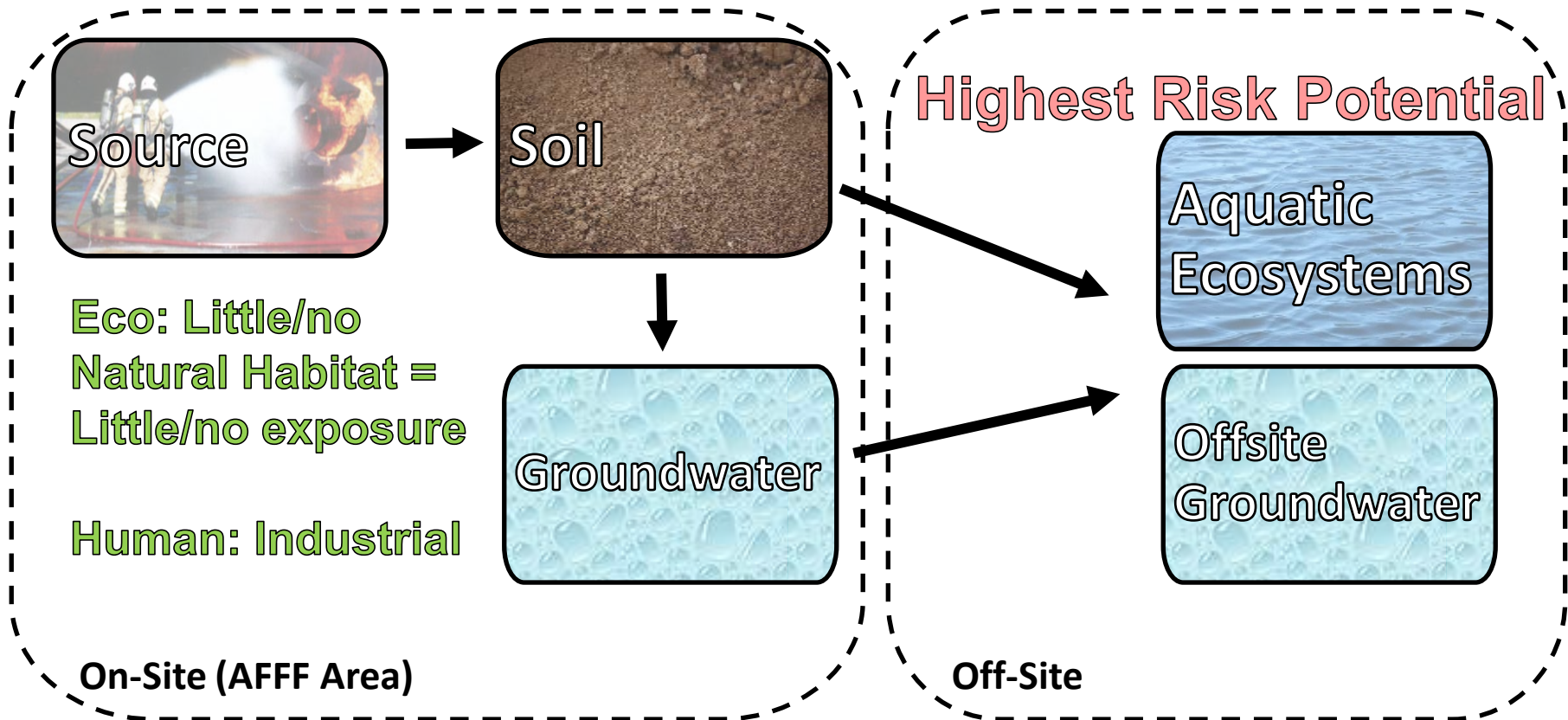
Conceptual Site Model for AFFF Risk



Conceptual Site Model for AFFF Risk



Conceptual Site Model for AFFF Risk

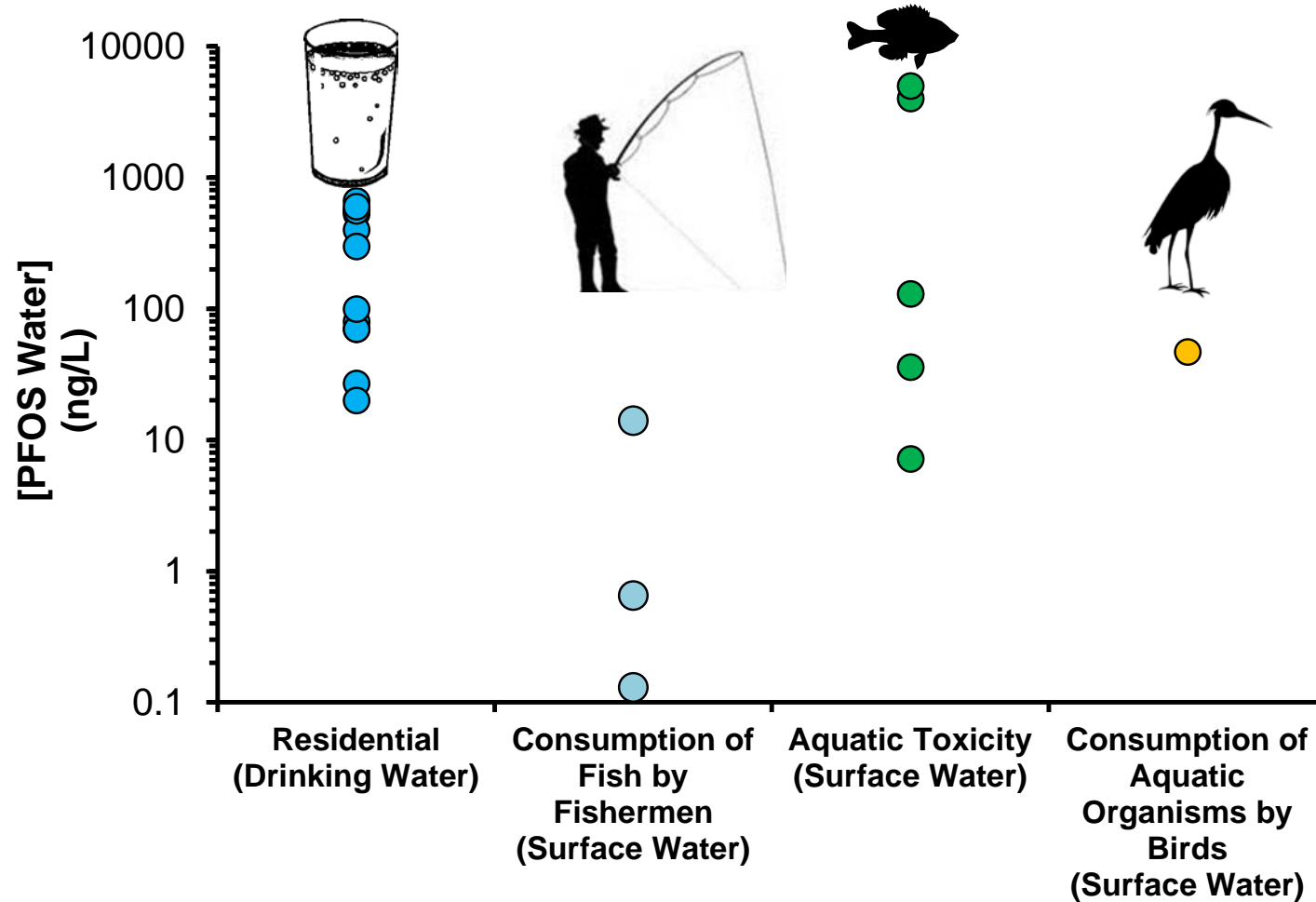


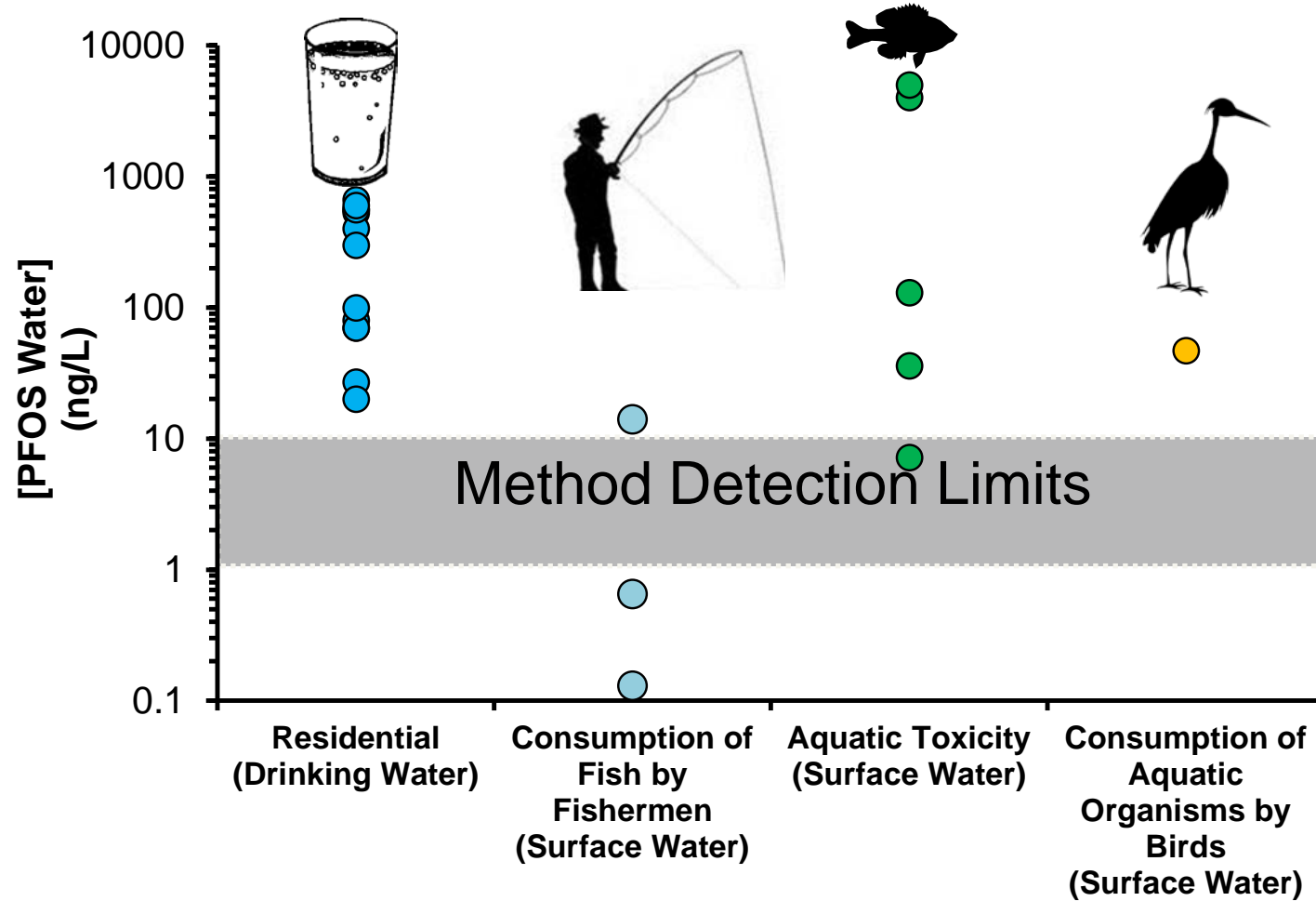
PFAS Toxicology and Risk Assessment

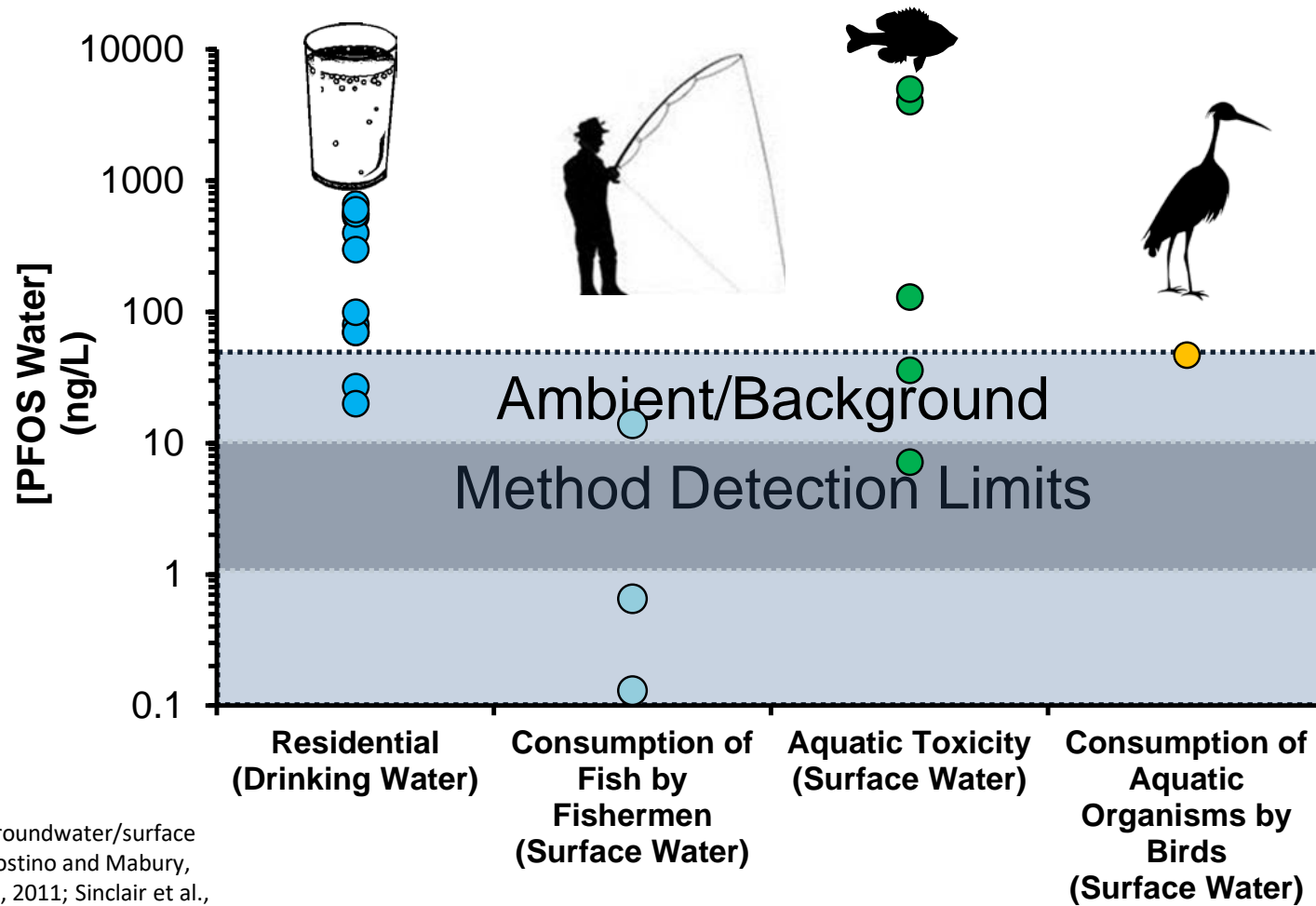


- **Most toxicology studies have focused on PFOA and PFOS**
 - Non-cancer effects in mammals are primarily focused on developmental effects
 - Immunotoxicity potential
 - Potential carcinogenic properties
 - “Suggestive” for both (USEPA) and “Possibly” for PFOA (International Agency for Research on Cancer)
- **Human health reference doses for PFOS and PFOA currently both 20 ng/kg body weight*day (USEPA)**
 - Some states have alternate values
- **Ecological**
 - Wildlife effects
 - Effects on liver and kidney
 - Reproduction
 - Aquatic toxicity data (fish, invertebrates) for some compounds
 - Plants and soil invertebrates not as sensitive

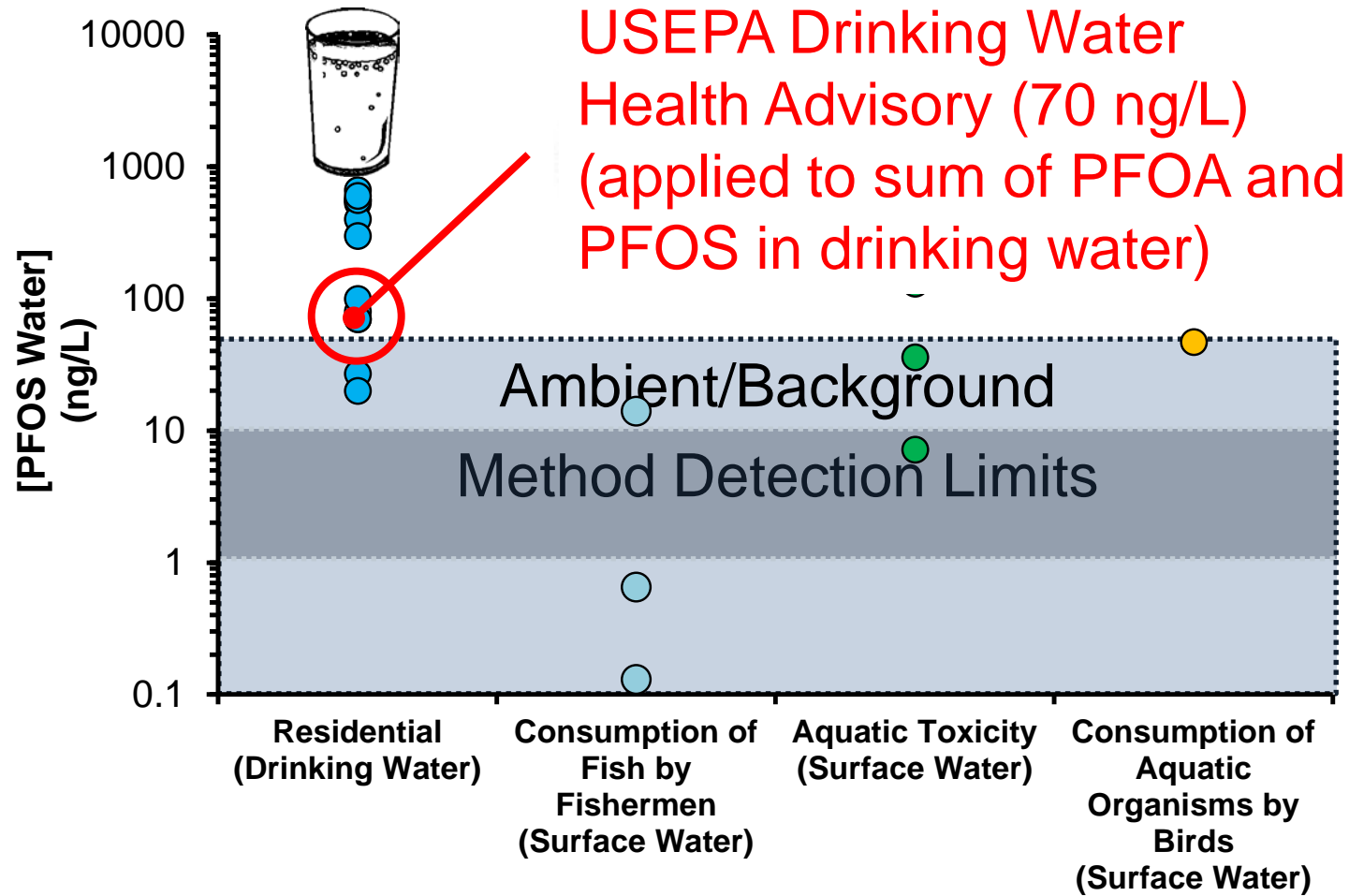
- Some information in peer-reviewed literature and chemical registration information
- Most focused on the PFCAs and PFSAAs, the perfluoroalkyl acid “families” to which PFOA and PFOS belong
- Effects generally similar (developmental, liver, kidney, etc.)
- Dozens to thousands of compounds







Ambient in groundwater/surface waters: D'Agostino and Mabury, 2017; Li et al., 2011; Sinclair et al., 2004; Konwick et al., 2008; Eschauzier et al., 2012; ATSDR, 2015



PFAS Regulatory and Management Landscape



- 2016 drinking water lifetime health advisory level for PFOS and PFOA (70 ng/L, PFOA+PFOS)
 - Advisory level, not a legally enforceable Federal standard
 - Supersedes the 2009 interim health advisory levels of 200 ng/L PFOS and 400 ng/L PFOA
- CERCLA
 - PFAS not yet CERCLA hazardous substances, so no cost recovery for Superfund (although they are considered a CERCLA pollutant or contaminant and can be investigated)
- Others
 - Site investigations and management driven by other forces, including: voluntary action (regulatory and public perception pressure), litigation, Clean Water Act (TMDL), variable approaches at state-level
- Risk assessment for PFOA and PFOS can be used as regulatory drivers
- Consult legal counsel – PFAS regulatory landscape will continue to evolve

- **USEPA path forward**
 - 2018 PFAS National Leadership Summit
 - Recognized PFAS as a national priority
 - “PFAS National Management Plan” will provide a roadmap
 - USEPA has initiated steps to evaluate the need for an MCL for PFOS and PFOA
- **US States are taking the lead...**



- **US States**

- Multiple (14) states currently have standards and guidance for PFOS and PFOA following EPA health advisory level

- Alabama, Arizona, Colorado, Connecticut, Delaware, Iowa, Maine, Massachusetts, Michigan, New Hampshire, Pennsylvania, Rhode Island, West Virginia

- Several states have standards and guidance that are more protective

- New Jersey MCLs: 14 ng/L PFOA, 13 ng/L PFOS
- Vermont primary groundwater enforcement standard: 20 ng/L PFOA, PFOS

- California

- Interim notification levels: 14 ng/L PFOA, 13 ng/L PFOS
- Response levels (recommend taking source offline): USEPA drinking water health advisory



- **US States**

- Nine states have assessment criteria for additional PFAS beyond PFOS, PFOA and PFHxS, including:
 - PFNA, PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOSA, PFDA, PFDS, PFUnA, PFDoA, PFTTrDA, PFTeDA
 - One state (North Carolina) has an assessment criterion for GenX, a replacement for PFOA
- A website tracking US-based PFAS contamination currently lists 180 sites across the US (<https://pfasproject.com/pfas-contamination-site-tracker/>)

- **Washington State banning PFAS in AFFF**
 - Bans the sale starting in July 2020 unless its use is required by federal law or if AFFF will be used by an oil refinery, oil terminal, or chemical plant for fire fighting
- **No room for scientific discourse?**
 - Non-PFAS foams don't work as well in putting out fires
 - What's in the non-PFAS foams?
 - Re-formulated AFFF (short-chain PFAS) not as harmful as original AFFF
 - Now that we know to control AFFF use carefully, can Best Management Practices be part of the answer?



- Remediation extremely challenging because most PFAS not bio- or chemically-degradable
- Current default/best approaches very expensive
 - Soil
 - Excavation and disposal (landfill)
 - Water
 - Pump & treat with activated carbon
 - Large volumes of carbon needed due to high water solubility of PFAS
 - Order of magnitude more expensive than pump & treat for VOCs
 - Systems optimized for VOCs not likely addressing PFAS



Carbon treatment systems to treat PFAS in water (MDH, 2012)

- A lot left to learn about PFAS
- Not just a human health drinking water issue
- Not just PFOS and PFOA
- Off-site issues are important
- Concentrations of PFAS at many sites can trigger concerns
- A lot of uncertainties and unanswered questions
- Site-specific risk assessment possible

For More Information...





ITRC Fact Sheets (draft/in development):

- Naming Conventions and Physical and Chemical Properties
- Regulations, Guidance, and Advisories
- History and Use
- Environmental Fate and Transport
- Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods
- Remediation Technologies and Methods
- Aqueous Film Forming Foam

▶ <https://pfas-1.itrcweb.org/>



ITRC Technical Resources for Addressing Environmental Releases of Per- and Polyfluoroalkyl Substances (PFAS)

PFAS Team Leaders:
Mueller, New Jersey Department of Environmental Protection
Lia Yingling, Minnesota Department of Health

ITRC PFAS Team Update
August 2018

v.itrcweb.org





ITRC Symposium on Characterizing and Managing PFAS at Impacted Sites

November 4, 2018

1:00 PM to 5:00 PM

Led by ITRC PFAS Experts

Location:

Sacramento Convention Center
1400 J St, Room 202
Sacramento, CA 95814

Travel Scholarships:

Available for state employees
from OR, NV, UT, ID, & AZ attending
this training. Please contact
Tadbir Singh at tsingh@ecos.org
or 202-849-4980 for details.

Who Should Attend?

State and federal environmental
and health agencies, tribes, local
governments, communities and others
interested in learning about PFAS.

FREE for state and federal
employees, academics, and
public stakeholders!

**Registration Fee for
Private Sector: \$10**

Register [**HERE**](#)

- Other 4- or 8-hour sessions being offered in other locations in the US over the next 4-6 months (contact me for details)



Thanks for Listening



Jason Conder
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