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

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Aqueous Film Forming Foam (AFFF)
Not snow!


Aqueous Film Forming Foam (AFFF)
Not snow!
Perfluoroalkyl and
polyfluoroalkyl substances
(PFAS)

Jason Conder

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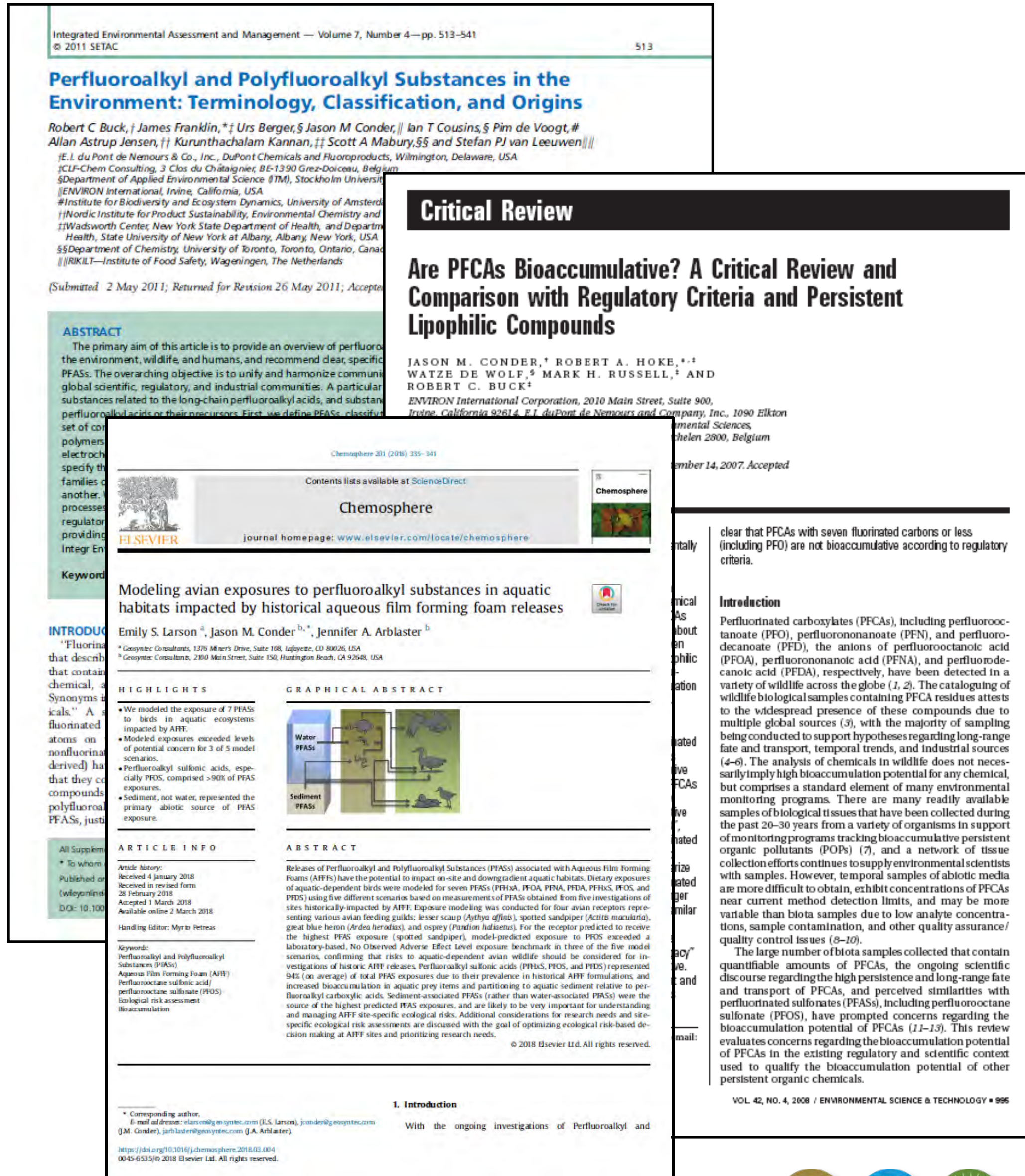
- PhD Environmental Toxicologist and Chemist
- PFAS site investigation and risk assessment
- Various PFAS projects since ~2005
  - 3 peer-reviewed papers on PFAS (chemistry, ecotoxicology, risk assessment)
  - US Department of Defense Frequently Asked Questions (FAQ) PFAS
  - US Department of Defense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



Overview

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- 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

What are PFAS?

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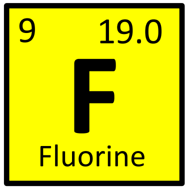
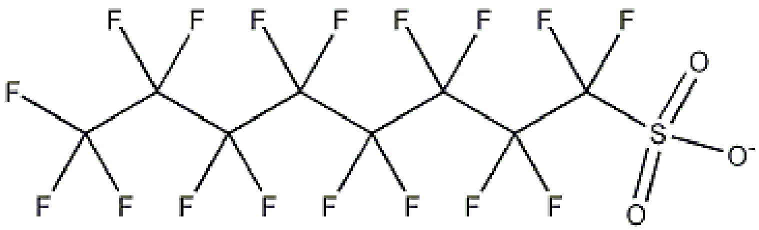
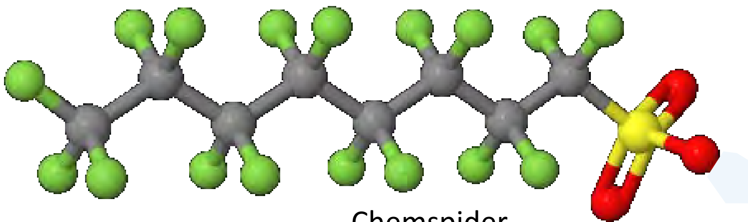
- PFAS: **P**erfluoroalkyl and **P**olyfluoroalkyl **S**ubstances
- A family of synthetic organic compounds that contain multiple fluorine (F) atoms





Conder et al. (2008)



Chemspider

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)

PFAS

- Hundreds-thousands of compounds

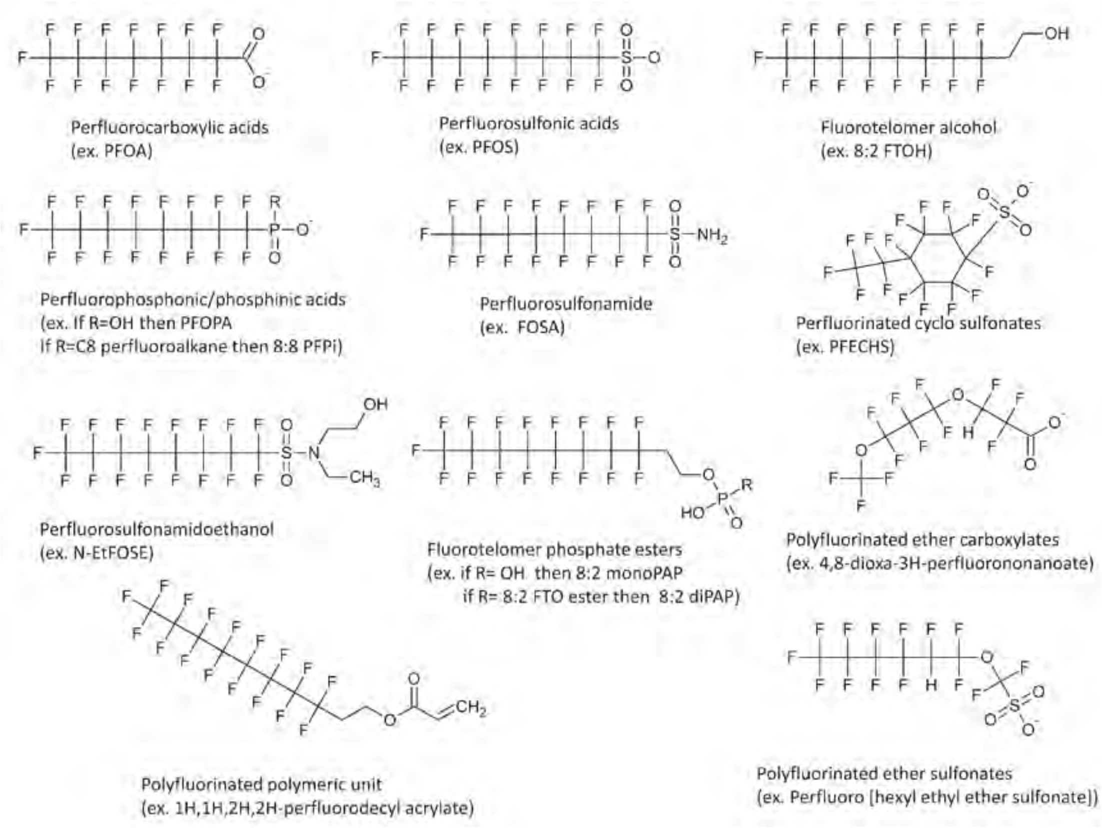
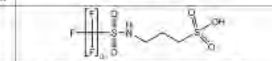
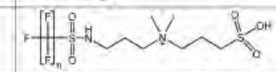
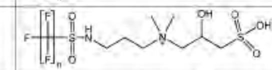
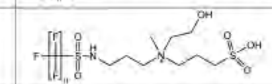
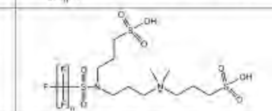
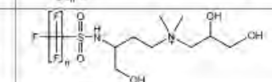
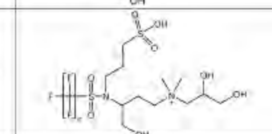
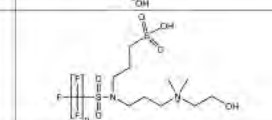
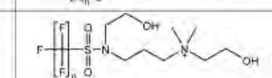
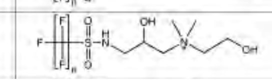


Table 1. Newly Discovered PFASs Found in AFFFs and CPs

Class Number	Structure	n[b,c]	Acronym[c]	Confidence Level[d,e]	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-SHOPAmP-FASA	3[f]	C, D, E, F, G
4		4-6	N-SPHOEAmP-FASA	3	B, C
5		3-8	N-SPAmP-FASAPS	2b	A, B, C
6		3-6	N-diHOPAmHOB-FASA	3	B, C, Q
7		2-6	N-diHOPAmHOB-FASAPS	3	A, B, C
8		2-8	N-HOEAmP-FASAPS	2b	A, B, C[e]
9		2-8	N-HOEAmP-FASE	2b	A, B, C, D, E
10		4-6	N-HOEAmHOP-FASA	3	B, C

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

Uses and Sources

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- 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 History

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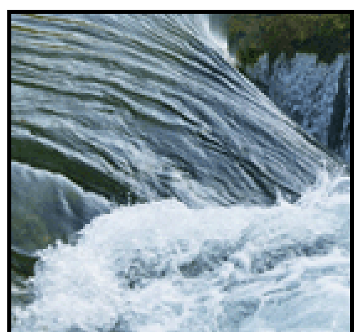
- AFFF = Aqueous Film Forming Foam
  - Complex, proprietary mixtures of fluorinated and hydrocarbon surfactants, water, corrosion inhibitors, solvent
  - ~1-10% PFAS by weight
  - 10s to 1000s of liters per use

- 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

AFFF Users

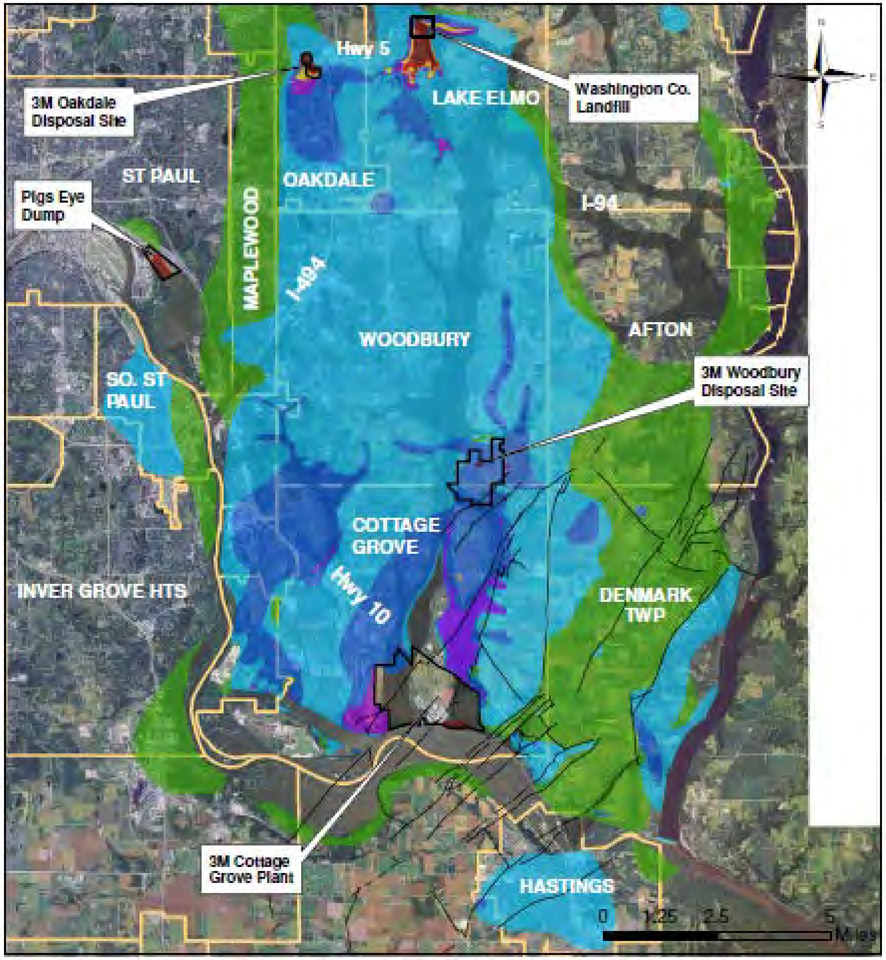
- 75% of AFFF produced was used by military
- Other AFFF users
  - Oil and gas industry
  - Bulk fuel storage
  - Chemical manufacturers
  - Airports
  - Municipalities
  - Landfills
  - Misc. (metal working industries, print industries, communities)



PFAS Fate and Exposures

Abiotic Environmental Fate

- 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 miles^2 (MDH, 2012)

Environmental Fate

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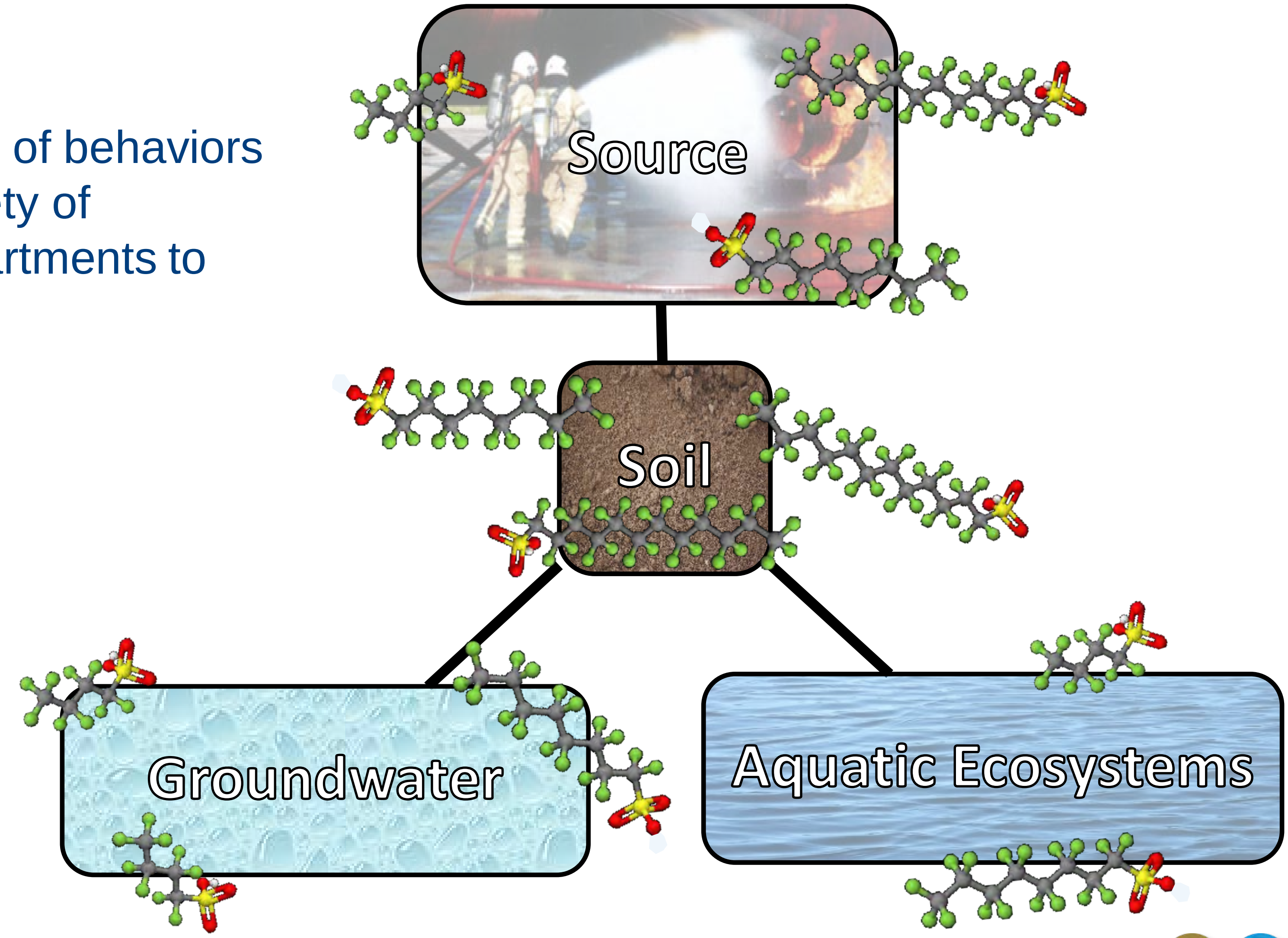
- Range of behaviors = variety of compartments to track



Biological Fate

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- 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)

BIOMONITORING CALIFORNIA 10TH ANNIVERSARY

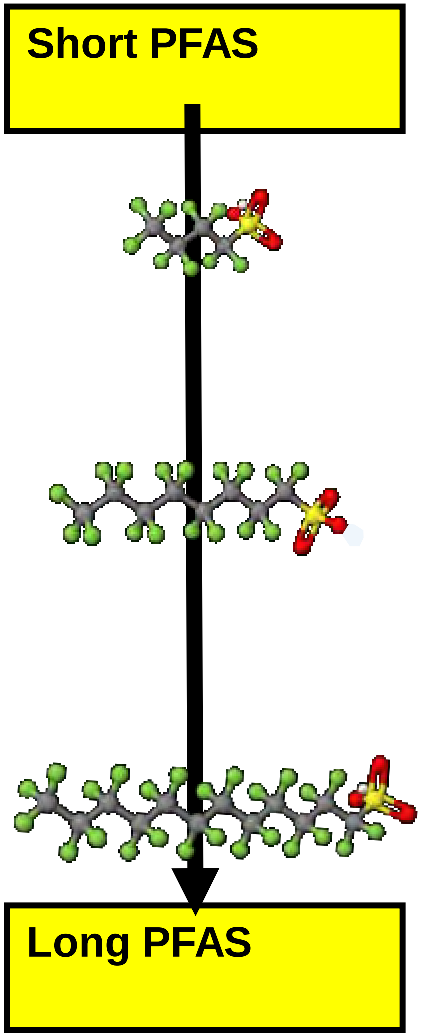
99% of California teachers with detectable PFAS

Chemical Group: Perfluorochemicals (PFCs)
› **Measured in:** Serum

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

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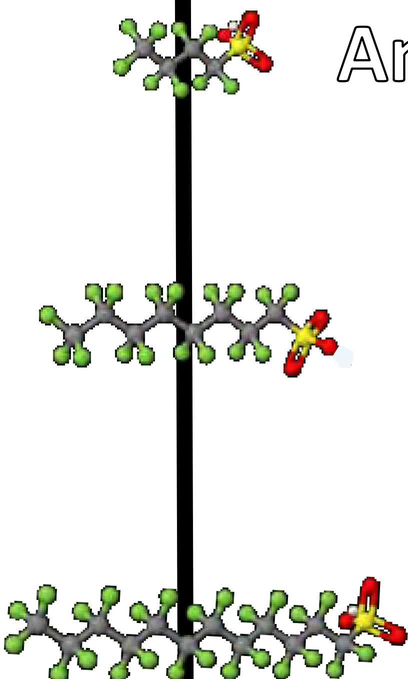
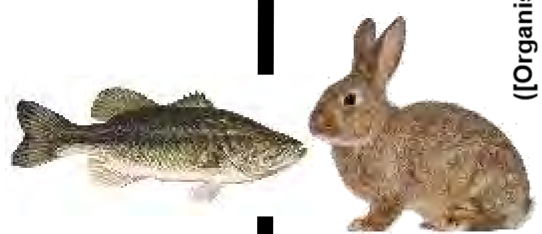
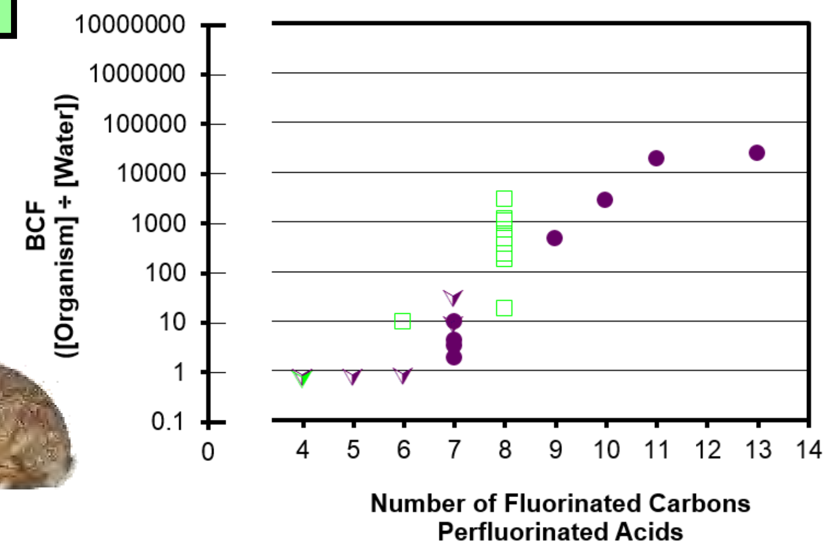
Short PFAS

Less bioaccumulative



Animals



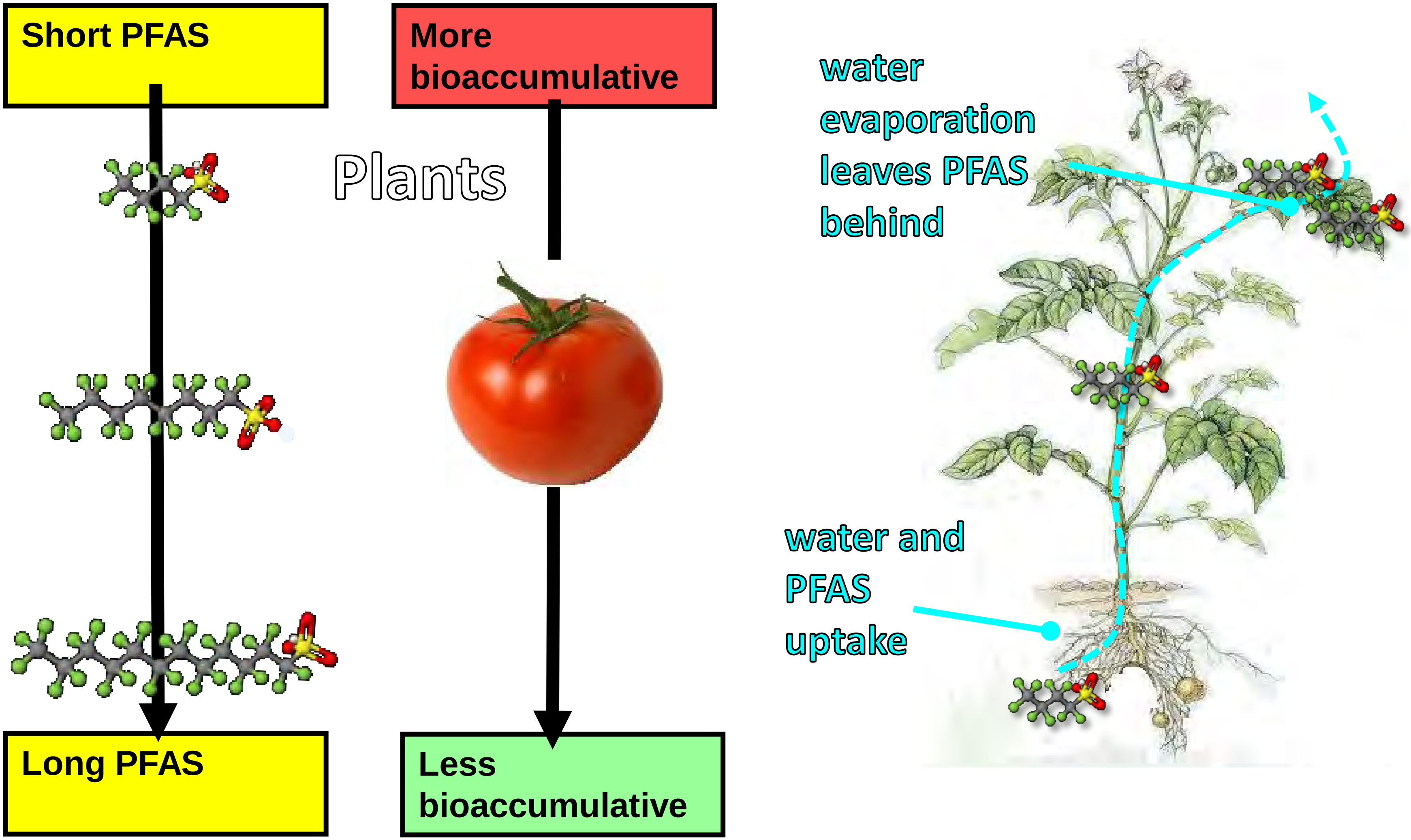


Conder et al. (2008) Environ. Sci. Technol. 42:995-1003

Long PFAS

More bioaccumulative

Chemical Size Affects Bioaccumulation



Human Exposure Pathways

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

PFAS in Municipal Drinking Water Supplies

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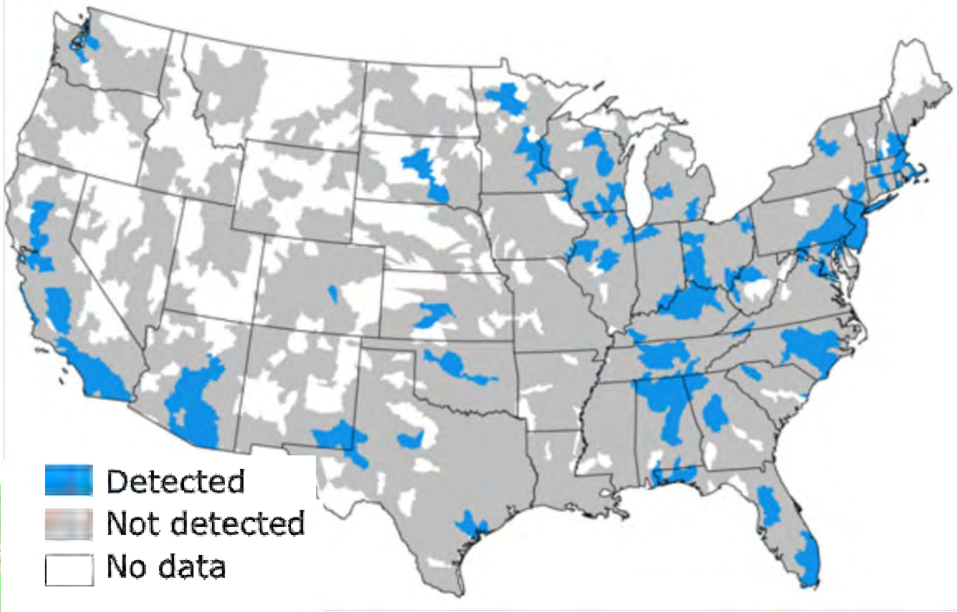
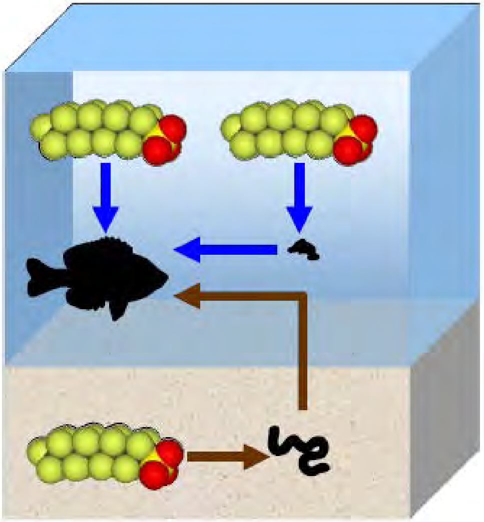
- PFAS detected above drinking water health criteria > 60 drinking water systems
  - EPA Unregulated Contaminants Monitoring program (UCMR3)

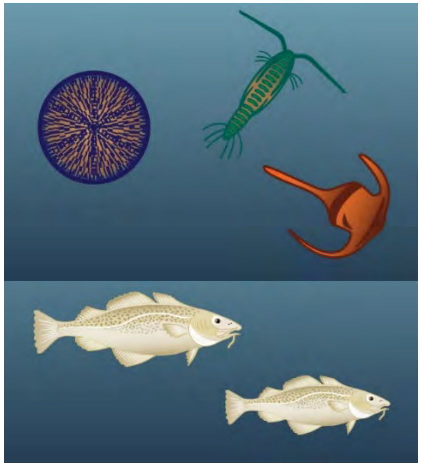


From Hu et al. 2016. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. ES&T Letters. 2016, 3 (10) pp. 344-350 (open access article). Copyright American Chemical Society.

Ecological Exposure Pathways

- 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

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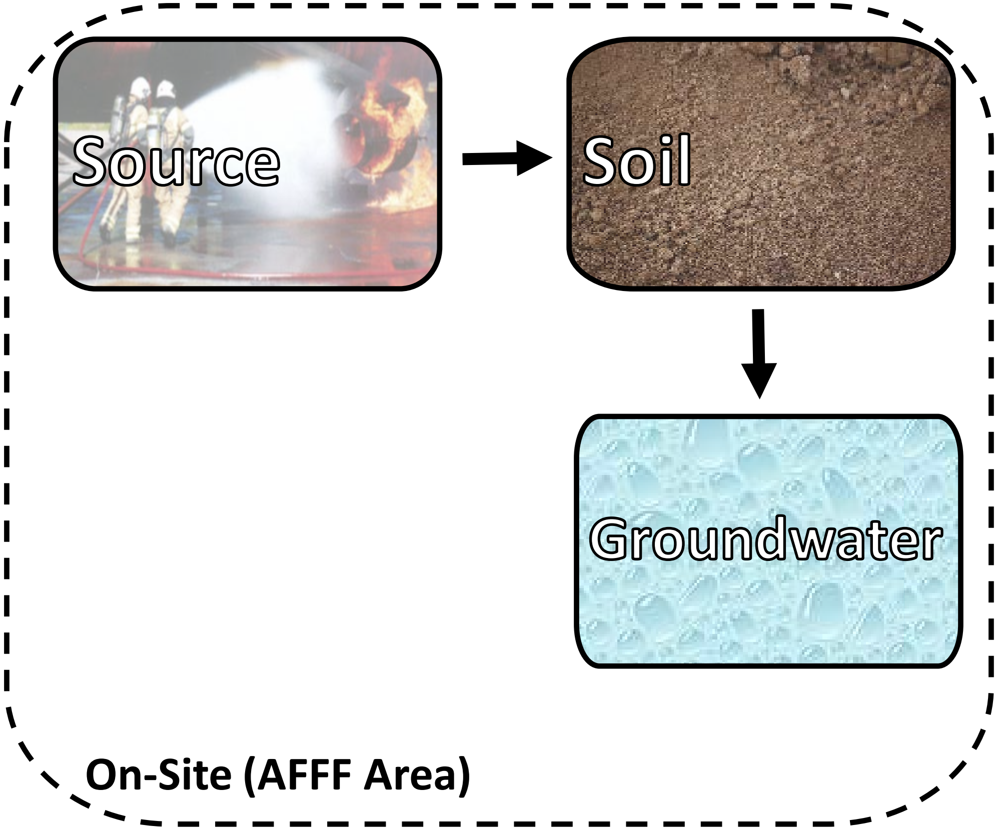
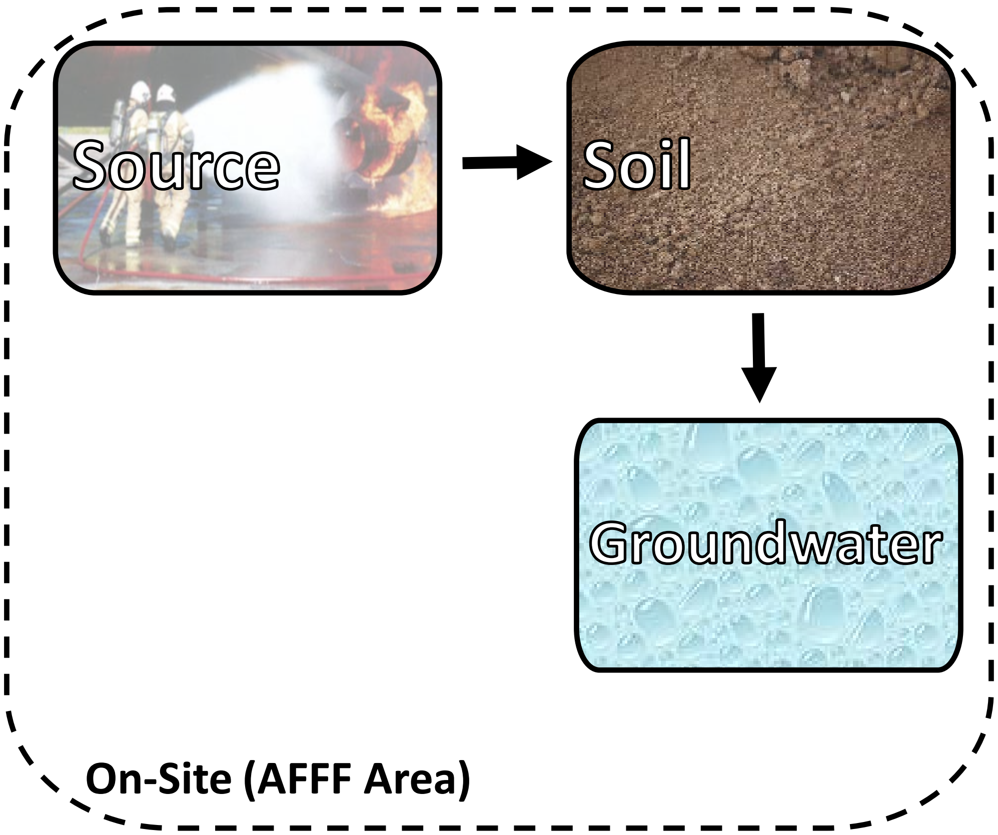


Conceptual Site Model for AFFF Risk



Conceptual Site Model for AFFF Risk

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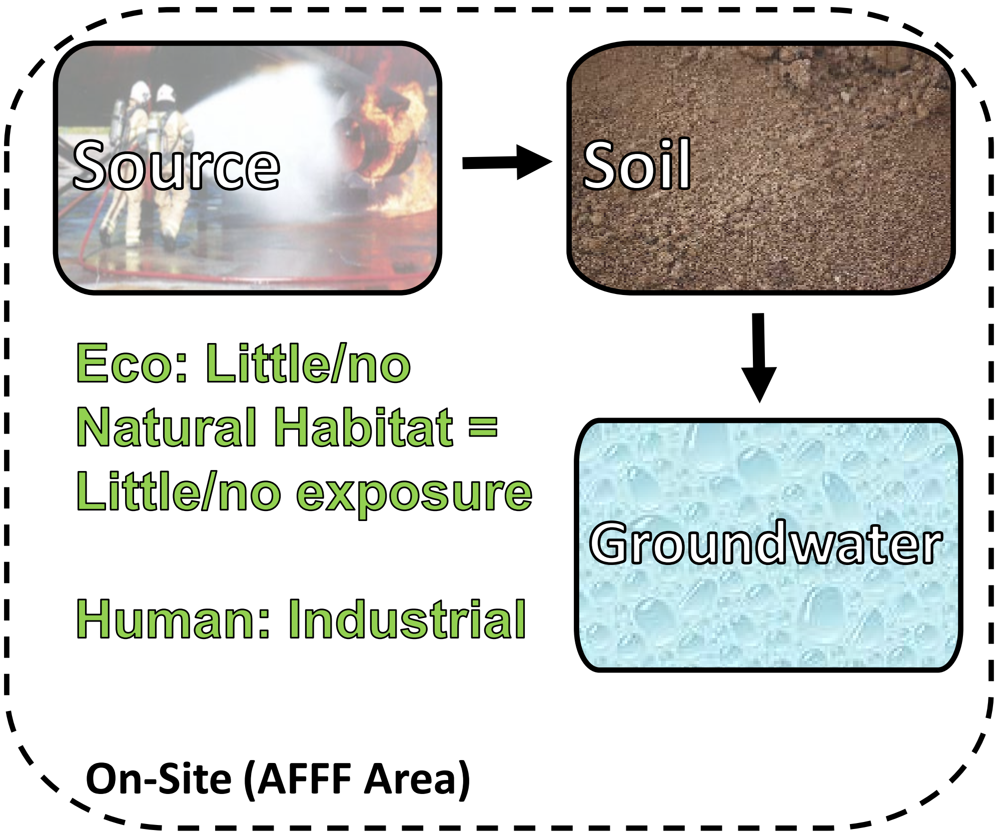

Conceptual Site Model for AFFF Risk

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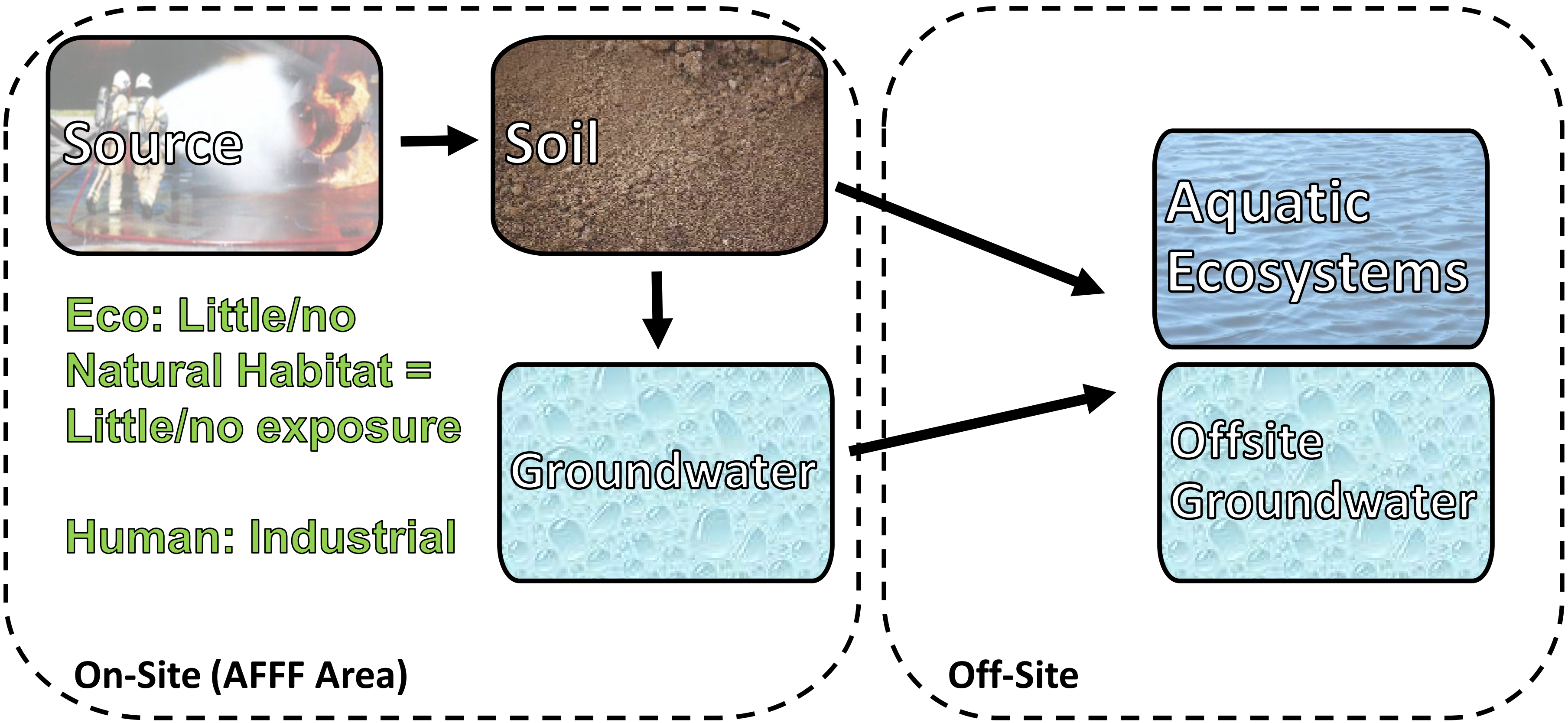

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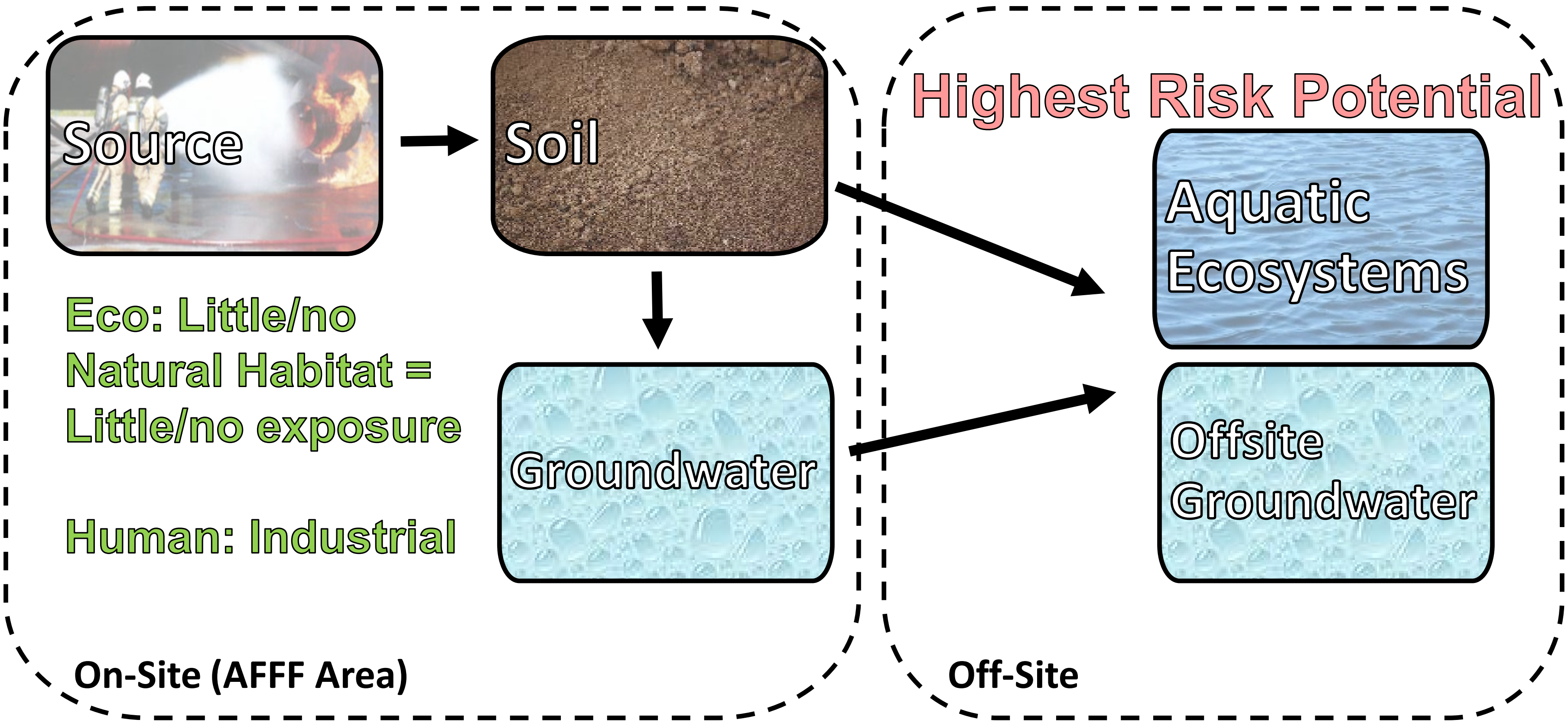

PFAS Toxicology and Risk Assessment

Toxicology of PFOA and PFOS

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- 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

Toxicology of Other PFAS

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

Example PFOS Risk-based Screening Criteria in Water

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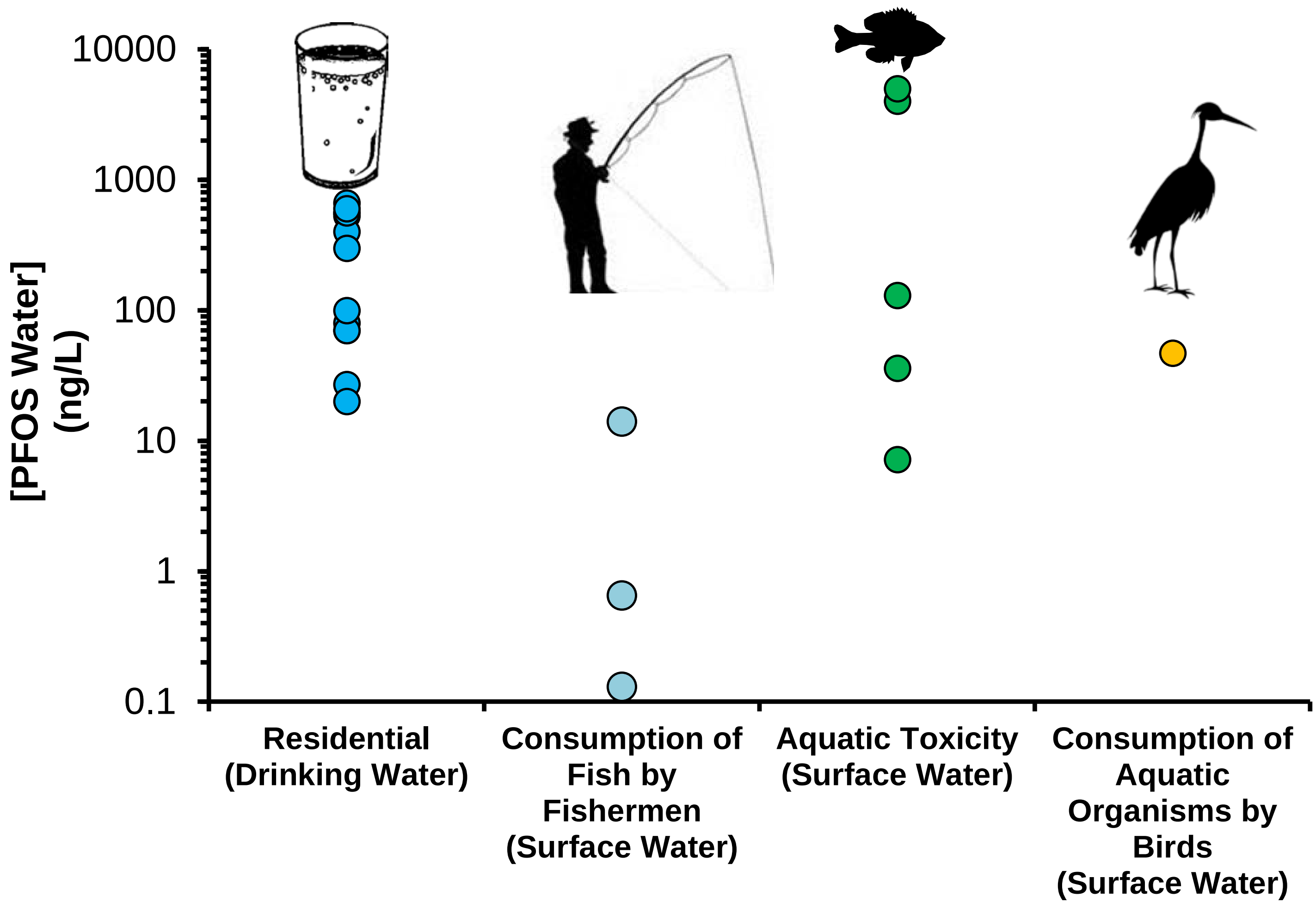
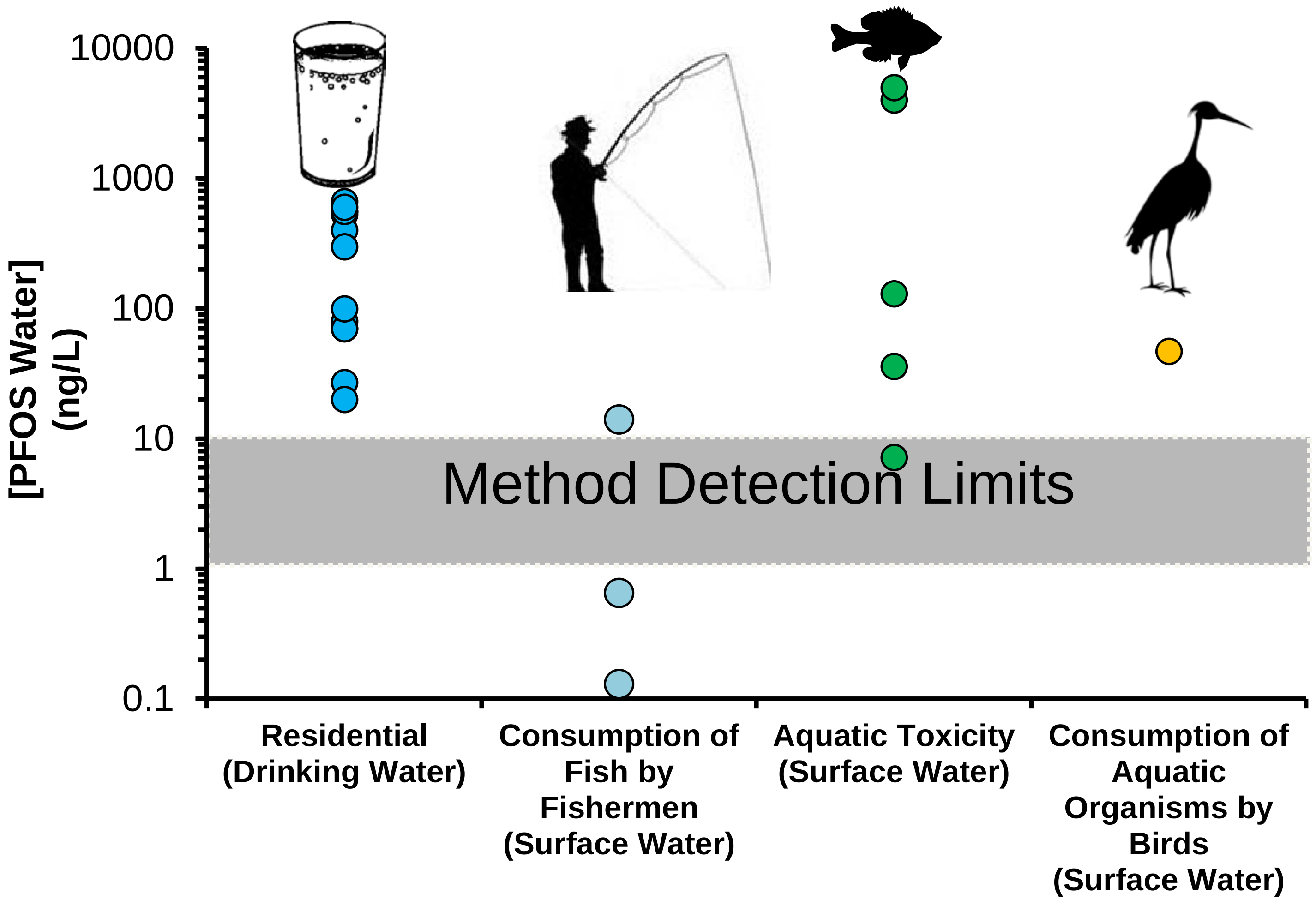


Example PFOS Risk-based Screening Criteria in Water



Example PFOS Risk-based Screening Criteria in Water

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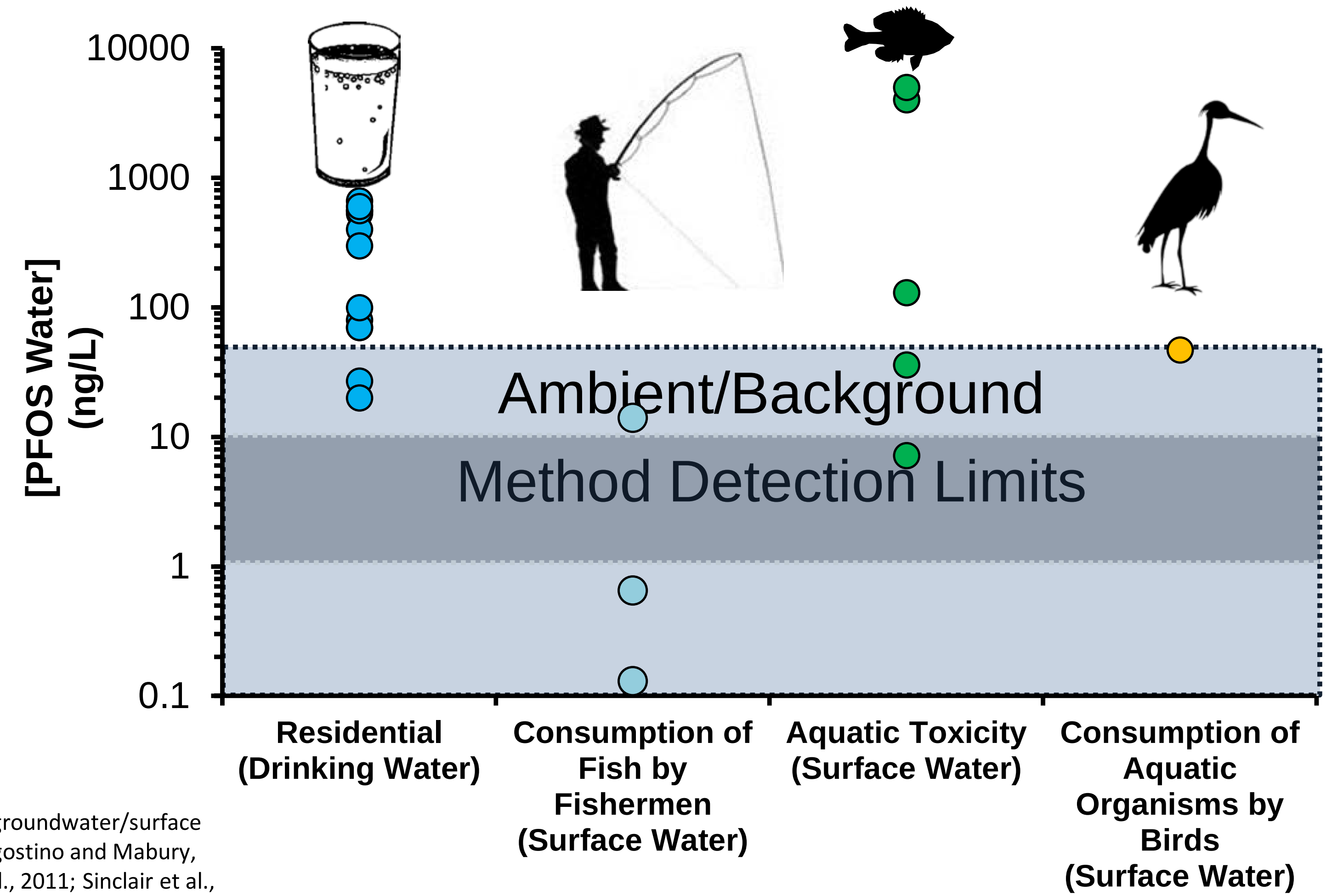
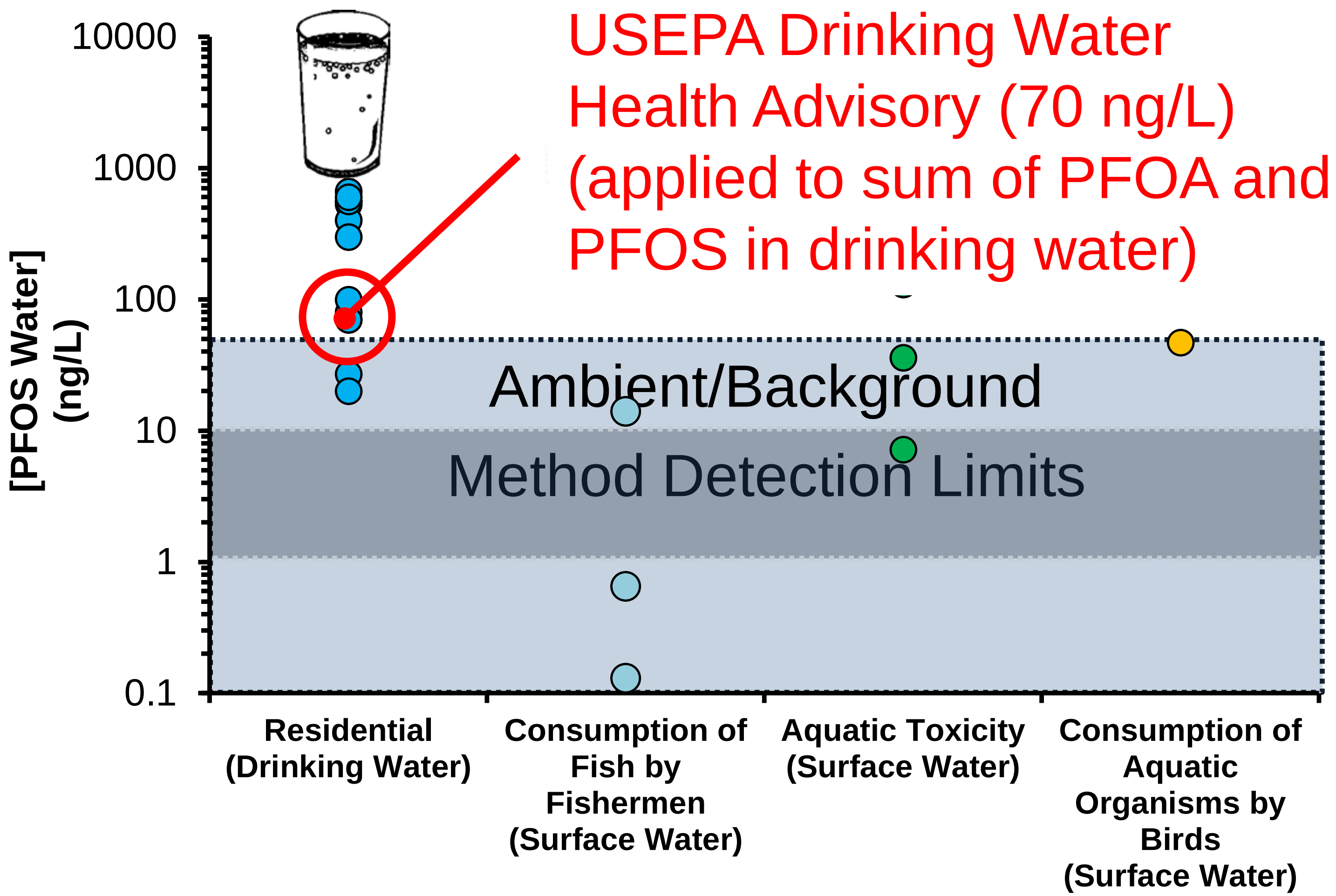


Ambient in groundwater/surface waters: D'Agostino and Mabury, 2017; Li et al., 2011; Sinclair et al., 2004; Konwick et al., 2008; Eschauzier et al., 2012; ATSDR, 2015

Example PFOS Risk-based Screening Criteria in Water



PFAS Regulatory and Management Landscape

PFAS Regulatory Drivers

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- 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

PFAS Regulations and Guidance

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- 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…

PFAS Regulations and Guidance

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- 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

PFAS Regulations and Guidance

- 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, PFTrDA, 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/)

PFAS Ban in AFFF

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- 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

- 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)

Conclusions

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- 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 PFAS Resource

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
ia Yingling, Minnesota Department of Health

ITRC PFAS Team Update
August 2018

v.itrcweb.org

4-hour Symposium, Nov 4, Sacramento, CA

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INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC

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***

PFAS

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ECOS

- 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

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