PFAS – What Are They, Why Do We Care, & What Are We Doing About Them?

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Minnesota Department of Health

DEPARTMENT OF HEALTH

What are Per- and Polyfluoroalkyl Substances (PFAS)?

- Large class of surfactants (>4000)
- Unique chemical & physical properties (oil-, water-, stain-repellent; thermally stable)
- Used since 1940s in many industrial processes, fire-fighting foams, and consumer products
- Some are extremely persistent & mobile in the environment – global distribution
- In the US - PFOS & PFHxS phased out by 2008; PFOA phased out by 2015
  - Some “exemptions”, existing fire-fighting foam stockpiles can be used, & some nations continue to make them
  - Replacement chemistries “should” be less toxic, but still have risks and many are even more soluble & mobile

Source: open access images – bing.com

Main PFAS Releases to the Environment

Source: modified from ITRC PFAS training slides, used with permission

The PFAS "Family Tree"

PFAS

Non-polymer ? Polymer

- Fluoropolymers - **example: Teflon©**
  Perfluoropolyethers (PFPE)
- Side-chain fluorinated polymers

The "forever" chemicals

Perfluorinated

PFAAs
PFCAs
PFSAs
FASAs

Perfluoroalkyl acids
- Carboxylates (eg. PFOA)
- Sulfonates (eg. PFOS)

Polyfluorinated

FTSAs
FTCAs
FTOHs
FASEs
FASAAs

Source: ITRC (2017) PFAS Naming Conventions and Physical and Chemical Properties factsheet

Source: open access images – bing.com

ABCs of PFAAs –

- **Perfluoroalkyl Acids (PFAAs) – the basic PFAS**
  - Fully fluorinated carbon chain or "tail"
  - Carboxylate (COO^-) or sulfonate (SO_3^-) "head"

4	B	(buta-)
5	Pe	(penta-)
6	Hx	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(nona-)…..

- **Perfluorinated = fully fluorinated** C_nF_{2n+1} - R
  - Won't degrade in the environment
- **Polyfluorinated = partially fluorinated** (e.g., O or H)
  - May degrade in the environment
- **C-F bond unbreakable in the environment**
  - Destruction only at high temperatures and/or high pressure

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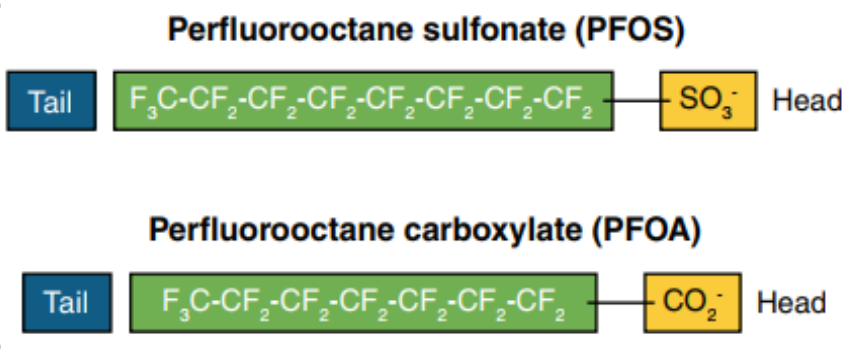

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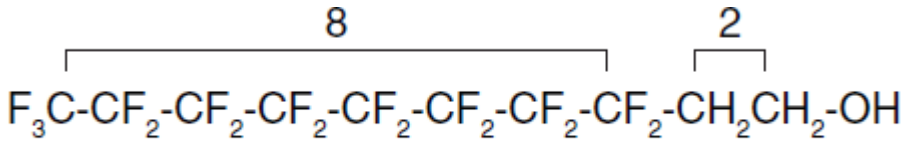


8:2 FTOH (8:2 fluorotelomer alcohol)

Source: ITRC (2017) PFAS Naming Conventions and Physical and Chemical Properties factsheet

PFAAs in the Environment

- Chain length and functional group help predict where PFAAs are most likely to be found

Little/no bioaccumulation **Bioaccumulate**

Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs		Long-chain PFSAs						

Source: ITRC (2017) PFAS Naming Conventions and Physical and Chemical Properties factsheet

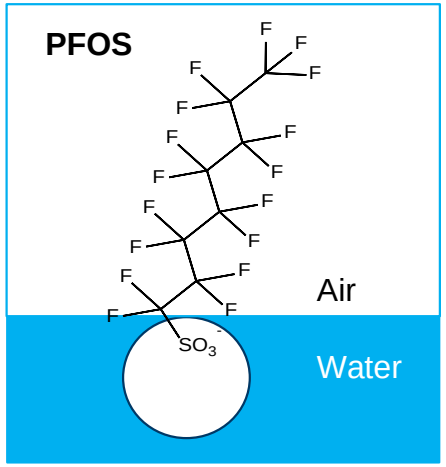
- Longer chain and/or sulfonate: relatively less water soluble & more bioaccumulative
  - Soils & sediments
  - Animals & humans

- Shorter chain and/or carboxylate: relatively more water soluble & less bioaccumulative
  - Surface water, groundwater, drinking water
  - Plants

- BUT: once in water all PFAAs are mobile to some extent

PFAAs in the Environment

- PFAAs are surfactants (like soap) – concentrate at air-water interfaces and bubbles

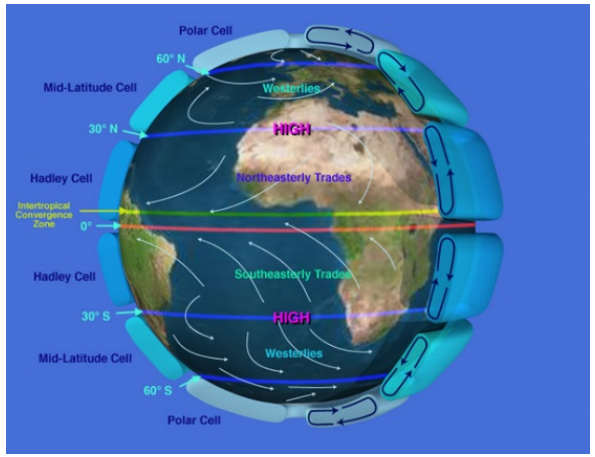


Used with permission from Jennifer Field, Oregon State University

Photos courtesy of MPCA

Water: low concentration (10 – 100's ppt)
Foam: high concentration (1-10,000's ppb)

- PFAAs generally have low volatility, however…
  - They can be on airborne particles or dissolved in water droplets
  - Some polyfluorinated PFAS are very volatile – and can transform to PFAAs that return to earth in rain or snow, or on dust particles



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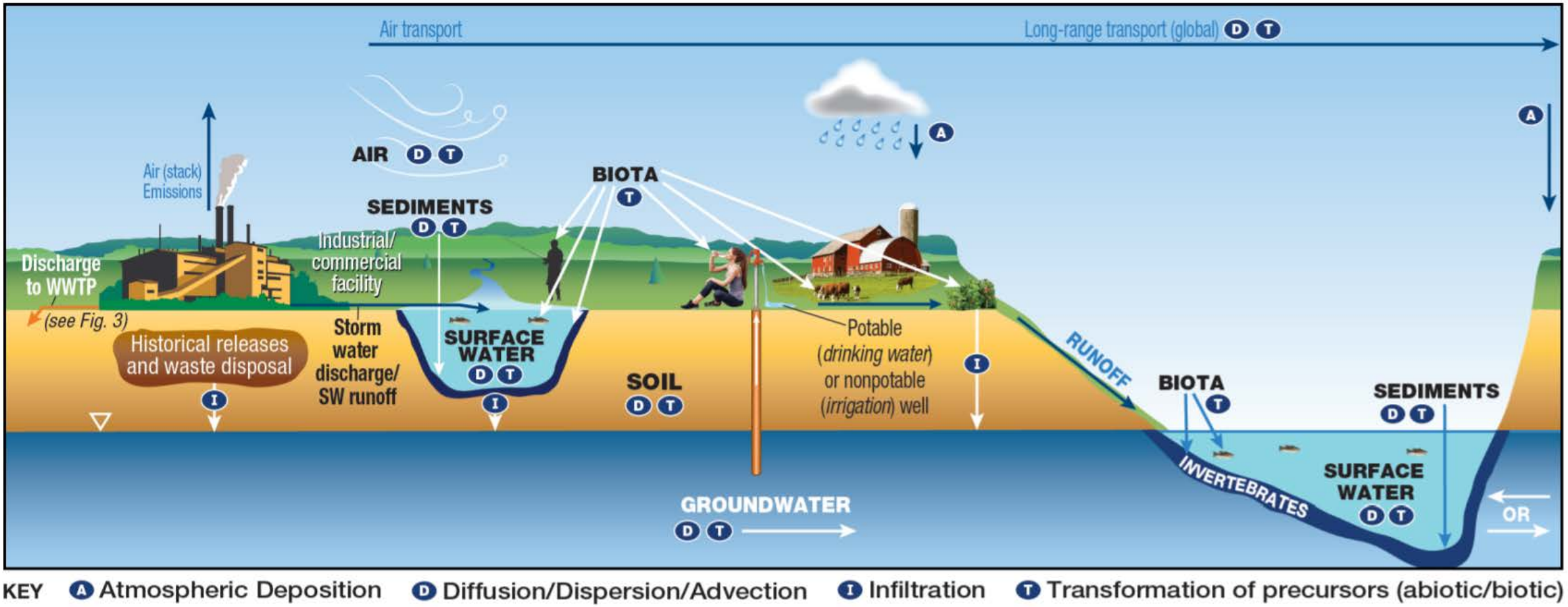
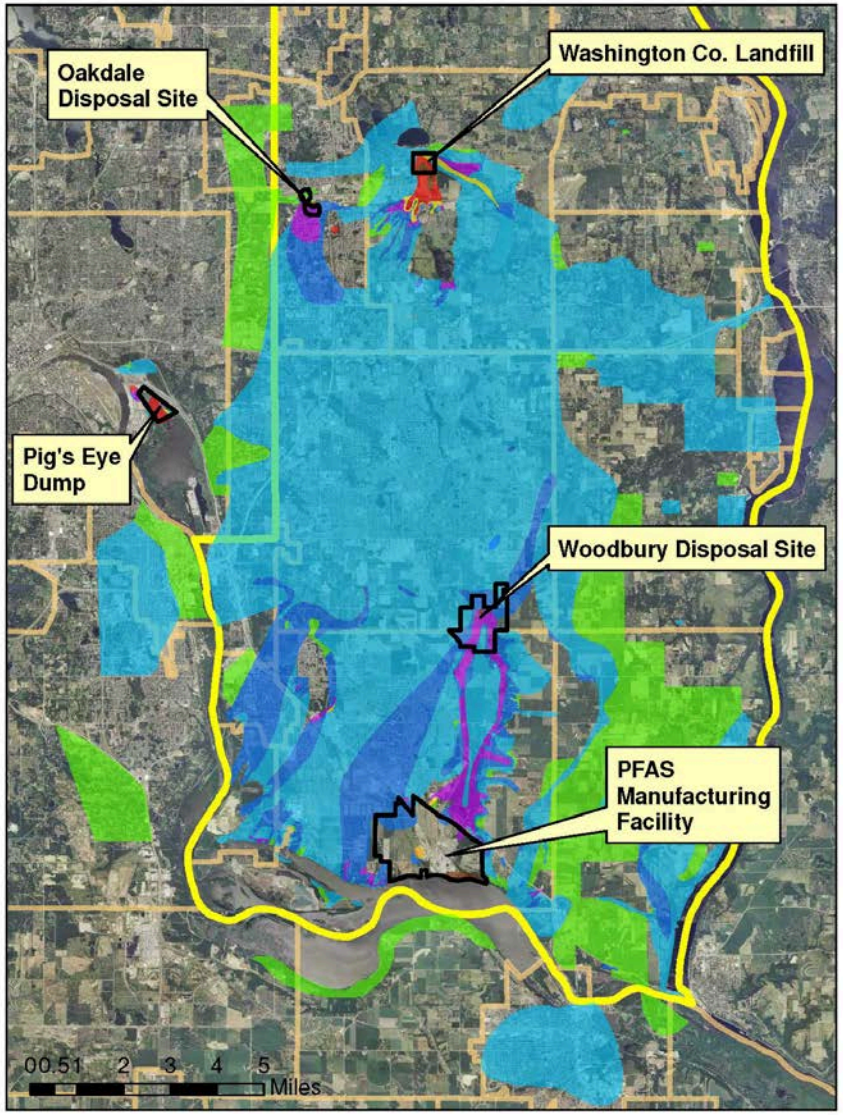
PFAS Environmental Fate & Transport



Source: ITRC Environmental Fate and Transport fact sheet, figure Adapted from figure by L. Trozzolo, TRC, used with permission

East Metro PFAS contamination

- PFAS manufactured since 1940s
- Waste disposal: on-site and landfills
- 2004 – PFOS & PFOA detected in Oakdale city wells
- Subsequent investigations:
  - >150 mi^2 contaminated GW & SW
  - 4 major aquifers
  - 13 communities
  - 8 municipal systems (140,000+ pop.)
  - >3,000 private wells (1,300+ advisories)
  - Additional sources: AFFF, WWTP sludge, illicit dumping, airborne deposition



Location of Legacy PFAS Sites in Washington Co., Minnesota

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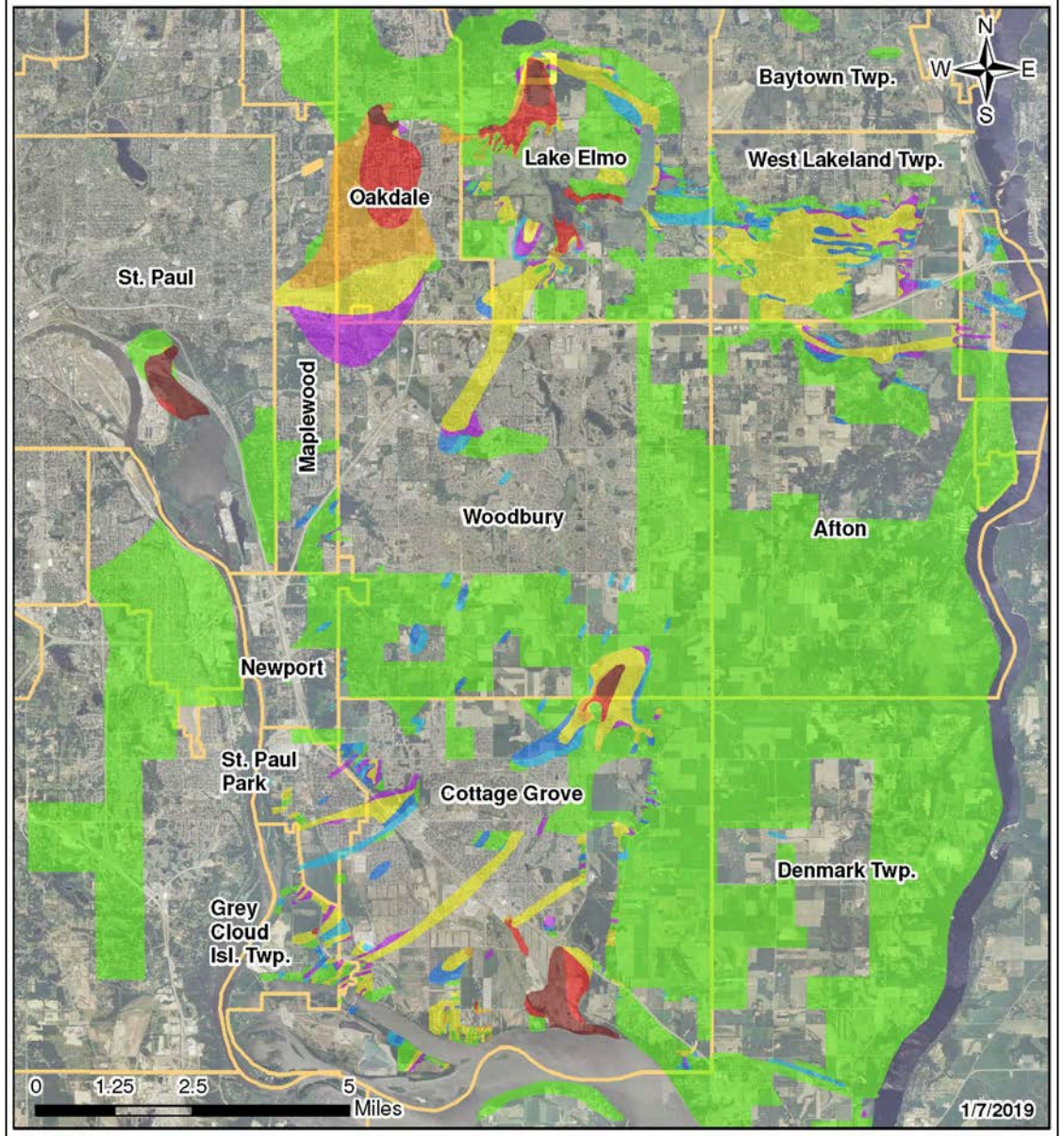
July 11, 2018



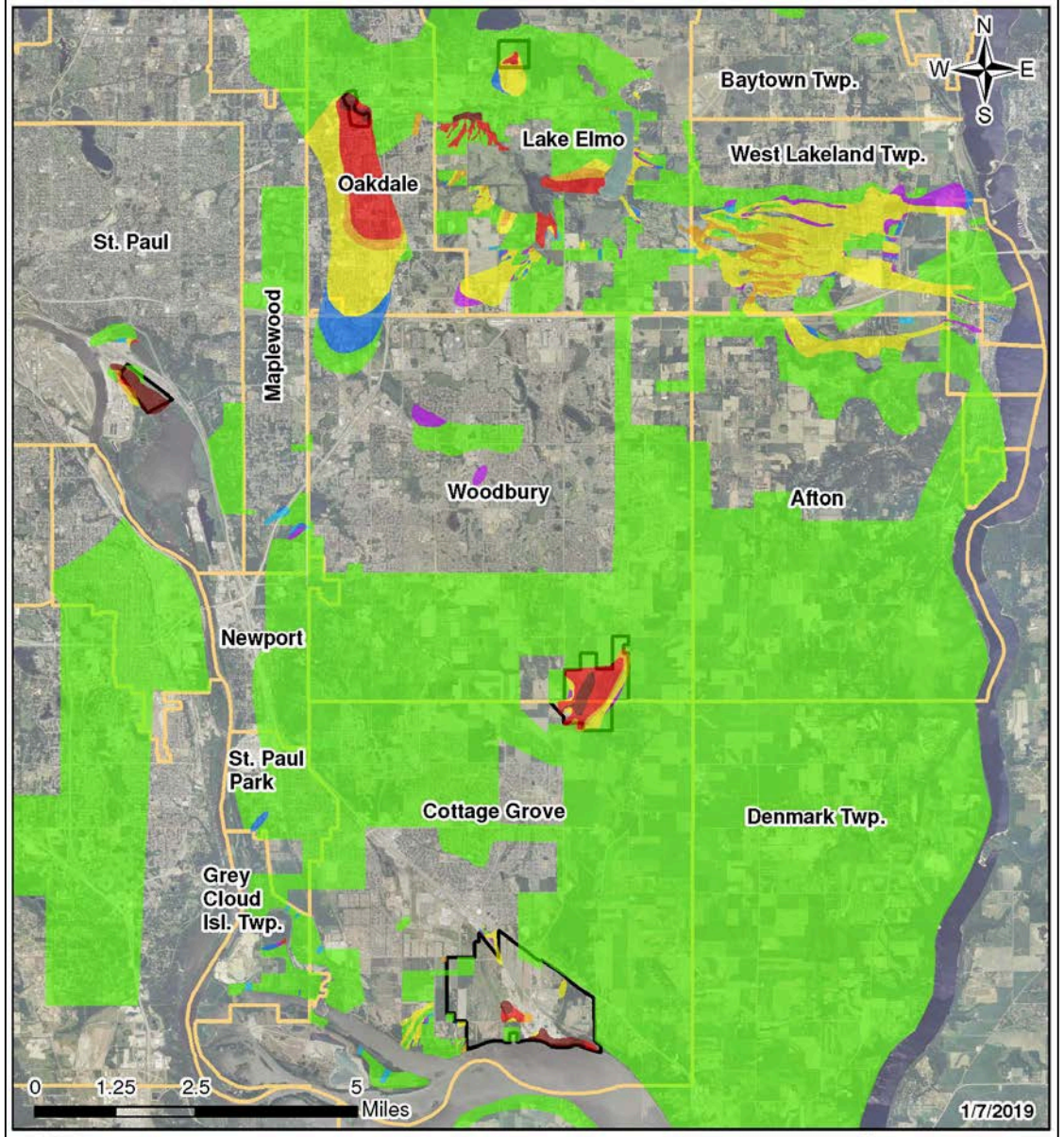
PFOA - All Aquifers

Phone: 651-201-4897
or 1-800-657-3908

- PFOA greater than 1.75 ppb (>50x HBV)
- PFOA 0.36-1.75 ppb (10-50x HBV)
- PFOA 0.176-0.35ppb (5-10x HBV)
- PFOA 0.036-0.175ppb (1-5x HBV)
- PFOA 0.027-0.035ppb (75-100% HBV)
- PFOA 0.0175-0.026ppb (50-75% HBV)
- PFOA 0.004-0.0174ppb (<50% HBV)
- PFOA not detected

MDH Health Based Value (HBV) for PFOA is 0.035 parts per billion (ppb; or 35 parts per trillion)

Map combines data from all aquifers - actual concentrations in any area may vary; blank spaces indicate no sample data



PFOS - All Aquifers

Phone: 651-201-4897
or 1-800-657-3908

- PFOS > 1.35ppb (>50x HBV)
- PFOS 0.271-1.35ppb (10-50x HBV)
- PFOS 0.136-0.27ppb (5-10x HBV)
- PFOS 0.028-0.135ppb (1-5x HBV)
- PFOS 0.021-0.027ppb (75-100% HBV)
- PFOS 0.0136-0.02ppb (50-75% HBV)
- PFOS 0.004-0.0135ppb (<50% HBV)
- PFOS not detected

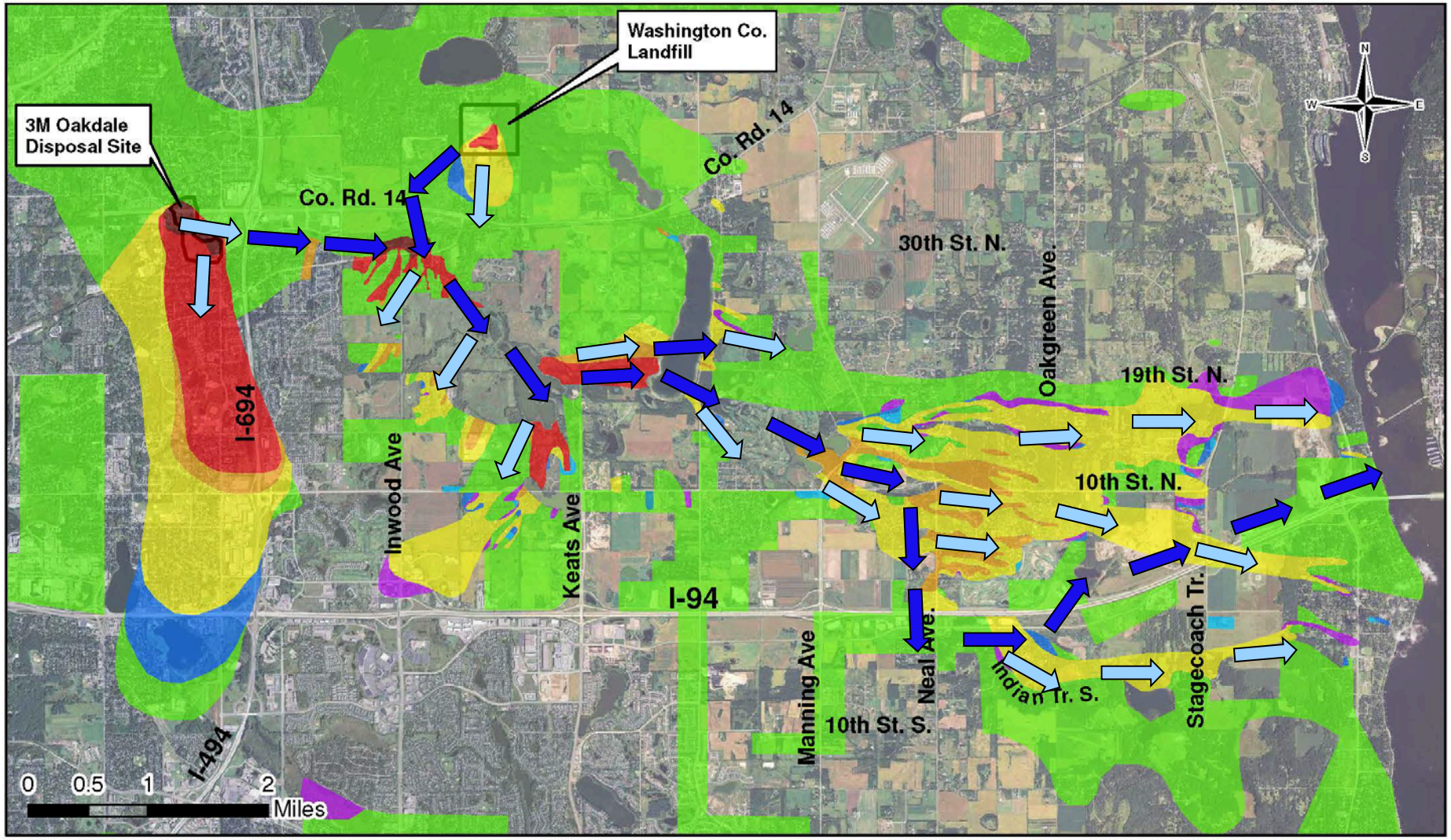
MDH Health Based Value (HBV) for PFOS is 0.027 parts per billion (ppb; or 27 parts per trillion)

Map combines data from all aquifers - actual concentrations in any area may vary; blank spaces indicate no sample data

Groundwater flow

Surface water or stormwater flow

- Surface water transport may move PFAS many miles away from source areas (See also: Awad et al., 2011 and Kwadijk et al., 2014).
- Infiltration along a surface water pathway may create discrete groundwater plumes isolated from the source.
- Groundwater discharge to surface water may contaminant water bodies distant from source areas.



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1/7/2019

Main Human Exposure Pathways

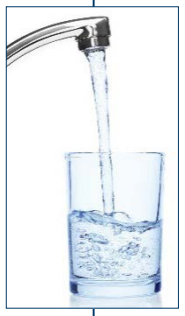
General Population

- Consumer products coated with PFAS
  - Textiles, carpeting, leather
  - Food contact packaging

- Diet (bioaccumulation)
  - Fish & seafood
  - produce

- Minor:
  - Incidental soil/dust ingestion
  - Skin contact w soil or consumer products

Near PFAS Sources



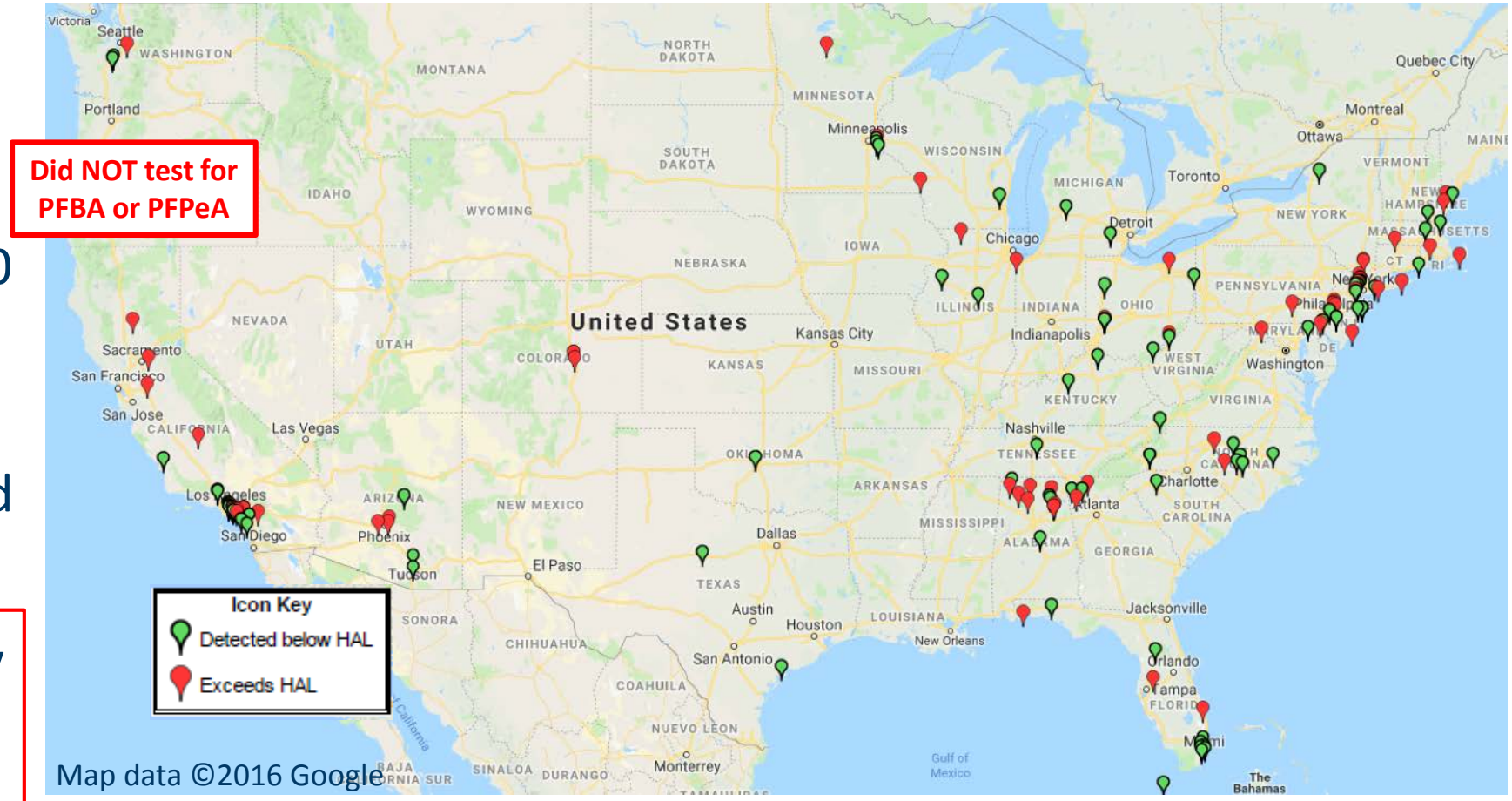
- Drinking water
  - ppt in water = ppb in serum

- Contaminated fish, animals
- Air emissions
- Minor:
  - Incidental soil/dust ingestion
  - Skin contact

PFAS in US Municipal Drinking Water Supplies

- 2013-2015 list included 6 PFAAs (PFOS, PFOA, PFNA, PFHxS, PFHpA, PFBS)
- Municipal systems >10,000 and selected smaller systems
- Detected in ~4%, exceeded EPA LHAs in ~1.3%
- High RLs and sampled only finished water at entry points, not wellheads or surface water sources

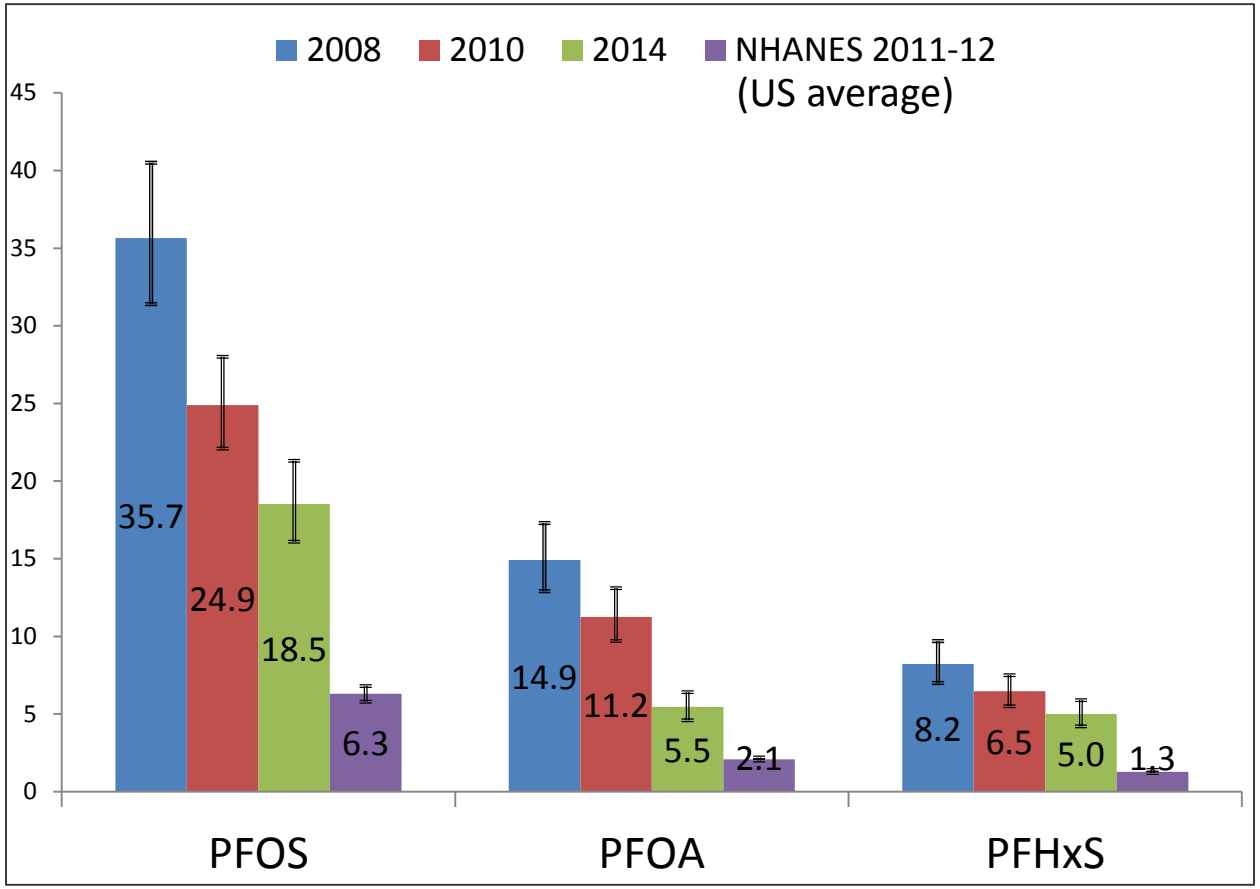
UCMR3: PFOS and PFOA Detections



Source: ITRC PFAS training slides, used with permission; figure used with permission from Andy Eaton, Eurofins-Eaton Analytical

Biomonitoring

- Exposed adults in affected East Metro communities:
  - 3 rounds: 2008, 2010, 2014
  - 196 initial participants (164 completed all 3 rounds)
- PFOS, PFOA, and PFHxS detected in 100%
- PFAS serum levels decreased for residents drinking treated water, but…
- Average concentrations > national average
- Conclusion: removing drinking water pathway key to reducing exposure



Health Effects of PFOA and/or PFOS

Animal (lab studies)

- ❑ Developmental effects
- ❑ Endocrine effects (thyroid)
- ❑ Immunological effects
- ❑ Liver effects
- ❑ Kidney
- ❑ Hematological (blood) effects
- ❑ Neurobehavioral effects
- ❑ Tumors (liver, testicular*, pancreatic*)

Sensitive endpoints: effects at lowest exposure levels

Human (possible links)

- ❑ Liver effects (serum enzymes/bilirubin, cholesterol)
- ❑ Immunological effects (decreased vaccination response, asthma)
- ❑ Developmental effects (birth weight)
- ❑ Endocrine effects (thyroid disease)
- ❑ Reproductive effects (decreased fertility)
- ❑ Cardiovascular effects (pregnancy induced hypertension)
- ❑ Cancer* (testicular, kidney)

*** PFOA Only**

Factors Impacting Numerical Values PFAS Drinking Water Guidelines

$$\text{Drinking Water Guideline} = \frac{\text{Reference Dose (mg/kg/day)} \times \text{Relative Source Contribution (\%)}}{\text{Drinking Water Consumption Rate (L/kg/day)}}$$

	Factor	Explanation	Examples	Impact
Reference Dose (POD ÷ Total UF; also includes animal-to-human extrap. factor)	Point of Departure (POD): • NOAEL • LOAEL • Benchmark Dose (BMDL)	Dose (mg/kg/day) from animal study used as starting point	• LOAEL for ↓ offspring body weight in rats • NOAEL for ↓ immune response in mice	↑ POD ↑ Guideline
	Uncertainty factors (UFs)	• POD is divided by individual UFs of 1-10 • Total UF generally 30-300	• Interindividual • Animal-to-human • Data gaps	↑ Total UF ↓ Guideline
	Animal-to-human dose extrapolation	To account for higher internal levels in humans than lab animals from same dose	• Serum PFAS levels as dose metric • Human-to-animal half-life ratio	Depends on specifics of approach
Exposure	Drinking water consumption rate	• L/kg/day. • Based on daily ingestion (L/day) and body wt. (kg)	• Infant > Lactating Woman > Default Adult • Predicts exposure to breast fed infant from mother exposed via drinking water	↑ Ingestion rate ↓ Guideline
	Relative Source Contribution (RSC)	Accounts for non-drinking water exposure sources (e.g. food, air)	• Default - 20% • 20-80% based on chemical-specific data	↓ RSC ↓ Guideline

Source: ITRC PFAS training slides, used with permission

Why are some states setting such low values?

- Longer chain PFAAs are highly bioaccumulative
  - Parts per trillion in drinking water = parts per billion in blood serum
  - Ongoing exposures = lifetime steady state concentrations
- Variable, age-based intake rates (IR) – much higher for infants
- Biological activity at very low exposures = lower “allowed” serum levels
- Significant potential exposure for babies born to exposed mothers
  - Placental transfer: PFOA ~60-200% of drinking water concentrations (ppt)
  - Breastmilk: PFOA ~2.6-12% of maternal serum concentrations (ppb)

PFOA & PFOS Guidelines and Standards (ppb)

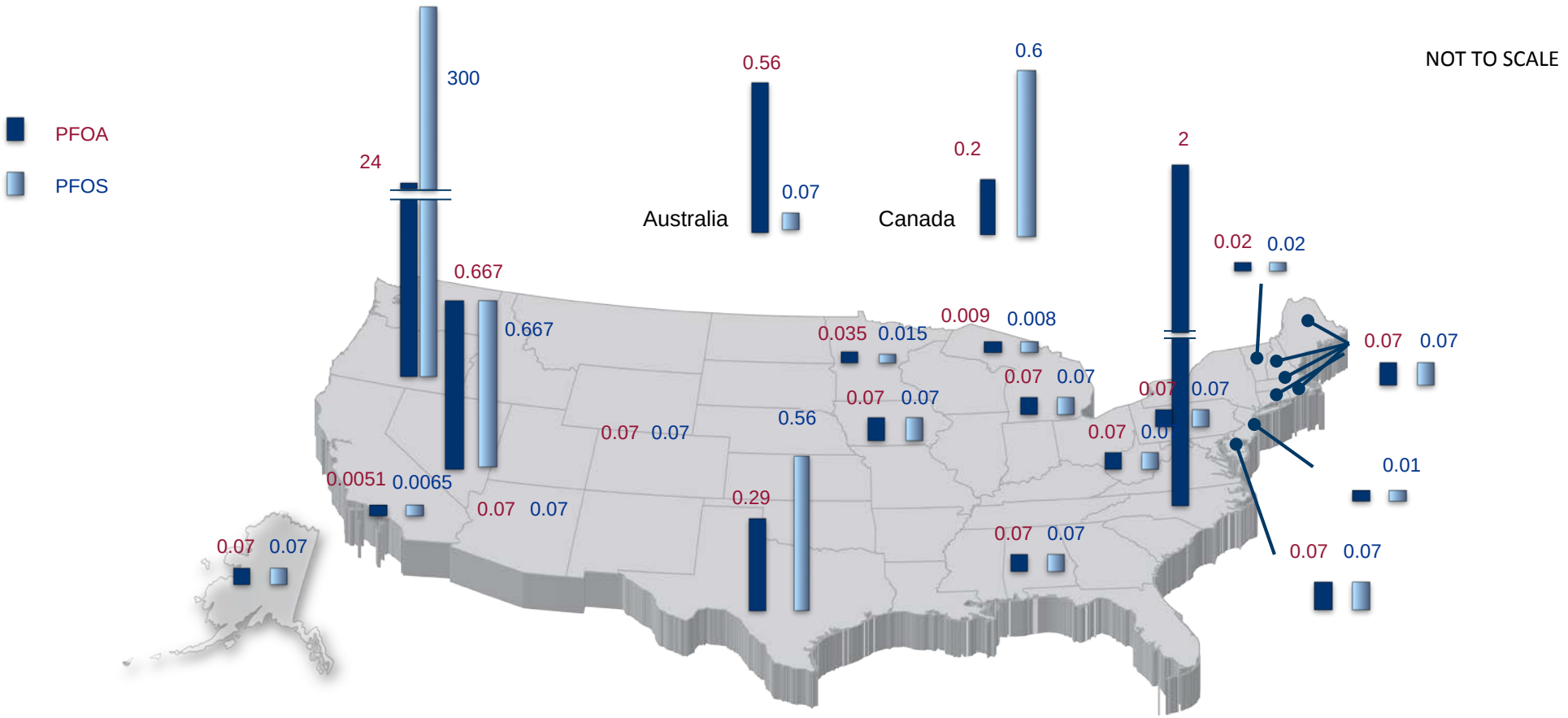


Figure by W. DiGuiseppi, Jacobs - used with permission. Data current as of October 2019
For current guidance values, see tables at https://pfas-1.itrcweb.org/fact-sheets/

What About Other PFAS?

- Fewer studies on other PFAS
  - Mainly PFCAs and PFSAs, but also “GenX” chemical HFPO-DA
- Similar health effects observed in animals
  - Long-chain health effects observed at low level (1-10’s ppt) exposures
  - Short-chain health effects observed at high level (100-1,000’s ppt) exposure
- USEPA to review five PFAAs for toxicity assessment (PFBA, PFHxA, PFHxS, PFNA, PFDA)
- Approaches other than “chemical by chemical”:
  - PFAS as a single class
  - Multiple classes (long-chain vs. short-chain)
  - High-throughput screening
  - Toxic Equivalency (similar to how mixtures of dioxins & PCBs are evaluated)

Regulatory Actions – US EPA

- Phase-outs of PFOA, PFOS, PFHxS and related chemistries (completed 2015, but some exemptions)
- Lifetime health advisories for PFOA and PFOS – not enforceable (MCLs being “evaluated”)
- Review new PFAS under Toxic Substances Control Act (TSCA) and issues Significant New Use Rules:
  - 1,223 listed in TSCA inventory > 602 are in active use > 400+ have SNURs
- Develop additional toxicity values
  - Finalize PFBS & “GenX”
  - New values for PFBA, PFHxA, PFHxS, PFNA, and PFDA
- Additional drinking water monitoring: UCMR5 (2015-2017), longer list
- Evaluate listing of PFOA & PFOS as CERCLA hazardous substances
- Explore adding some PFAS to the Toxics Release Inventory (TRI)
- Explore setting Clean Water Act ambient water quality criteria

Regulatory Actions – Other Federal Agencies

- FDA regulating certain PFAS in food-contact packaging and banned 3 perfluoroalkyl ethyl compounds
- FAA Reauthorization Act, 2018 – allows non-DOD airports to use foams other than AFFF (effective 2021)
- DOD replacement of legacy AFFF with “modern” AFFF (short-chain PFAS chemistry)
- DOD (SERDP/ESTCP) research on fluorine-free foam and other aspects of PFAS (fate & transp, analysis, treatment)
- ATSDR Draft Toxicological Profile – Minimal Risk Levels for PFOA, PFOS, PFHxS, PFNA

Legislation

Many small Bills introduced related to PFAS

- New MCLs – Protect Drinking Water from PFAS Acts (HR.2337, S.1473)
- CERCLA Hazardous Substance – PFAS Action Acts (HR.535, S.638)
- Additional TSCA prohibitions – Toxic PFAS Control Act (HR.2600), Protecting Communities from New PFAS Act (HR.2596)

National Defense Authorization Acts (NDAA)

- Includes many requirements from smaller bills as amendments
- Senate version (S.1790) – passed on 6/27/19 (86 - 8)
- House version (HR.2500) – passed on 7/12/19 (220 - 197)

Regulatory Actions - States

- Drinking water, groundwater, surface water, soil, and fish consumption guidance values or standards
- Product labeling & consumer protection laws
- Product bans (food packaging, AFFF, etc.)
- Hazardous substance designations
  - Restrictions on landfills
- AFFF take-back programs
- Occurrence studies
  - Release sources - industry, AFFF sites, WWTPs, landfills, land application, etc.
  - Ambient sampling – drinking water & environmental media (surface water, soil, fish, etc.)