

Poly- and Perfluoroalkyl Substances (PFAS) in Minnesota: An Update on the Chemicals Formerly Known as PFCs

Minnesota Groundwater Association

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Poly- and Perfluoroalkyl Substances (PFASs)

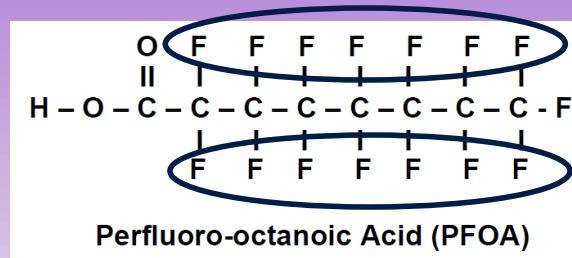
- Large class (200+) of surfactants with unique chemical properties
 - Fluorinated carbon chain with various functional group(s)
- Used since 1940s in products that resist heat, stains, water, oil and grease; production increased rapidly in 1970s
- Many other specialized industrial and commercial uses (operative word: non-stick)



What's With The New Name?

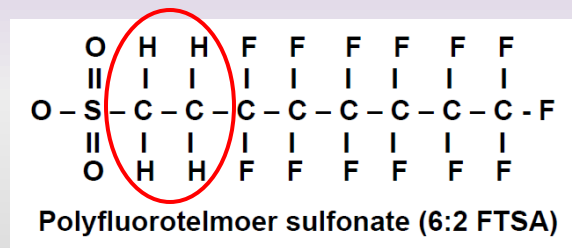
- Perfluoro-** means “fully” fluorinated

- All carbons in the chain bonded only to F
- These are actually “PFCs”
- Example: PFOA, PFOS, PFBA, PFBS, etc.
- Essentially non-degradable due to strength of C-F bond



- Polyfluoro-** means “partially fluorinated”

- Some carbons in the chain bonded to H
- Example: 6:2 FTSA (polyfluorotelomer sulfonate; 6 CF_2 , 2 CH_2)
- Susceptible to degradation (biotic and abiotic) due to weakness of C-H bond
- Some polyfluoroalkyl substances may degrade to PFCs
- May constitute the majority of PFASs at many sites, but typically not tested for

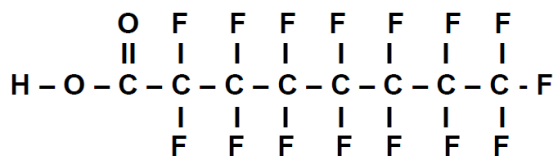


Just the Tip of the Iceberg?

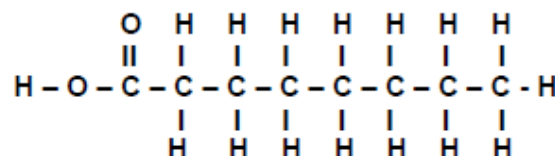
- **Current “targeted” analyte lists reportedly miss 80-90% of PFASs at some sites**
- **New methods being developed:**
 - **Total oxidizable precursor (TOP) assay - quantifies precursors (total PFASs) in groundwater, sediment, soil**
 - **Particle-Induced Gamma Ray Emission (PIGE) – measures total fluorine, but high detection limits and best used as screening tool.**
- **New Questions/Issues:**
 - **Are undetected precursors acting as on-going sources of PFCs?**
 - **How do we respond to detection of even more PFASs for which we have no eco- or human health risk information?**

PFCs Behave in Unique Ways

- **Do not break down in the environment**
 - No hydrolysis, photolysis, or biodegradation
- **Do not adsorb readily to aquifer materials**
 - Infiltrate rapidly to the groundwater
 - Little or no retardation
 - Rates affected by PFC chain length and functional group → partitioning
 - Carboxylates (PFBA, PFPeA, PFHxA, PFOA) – prefer water
 - Sulfonates (PFBS, PFHxS, PFOS) – prefer soil and sediment
- **Chemical structure similar to fatty acids**
 - Readily adsorbed into blood serum of living organisms



Perfluoro-octanoic Acid (PFOA)



Caprylic Acid

PFASs In The News Again

UCMR3 – Unregulated Contaminant Monitoring

- PFOS, PFOA, PFBS, PFHxS, PFHpA, PFNA (not PFBA)
- Sampled “entry point” (so some samples blended)
- PFAS detected in 20 states:
 - PFOS: 1.9% of PWS
 - PFOA: 2.2% of PWS
 - “High” reporting limits (10-90 ng/L) = under-reporting?
 - Eurofins – Eaton Analytical data mining suggests PFOS and PFOA may be present in ~20% and PFHxS in ~10% of PWS (2.5 – 5 ng/L)

UCMR3 PFOS-PFOA Detections

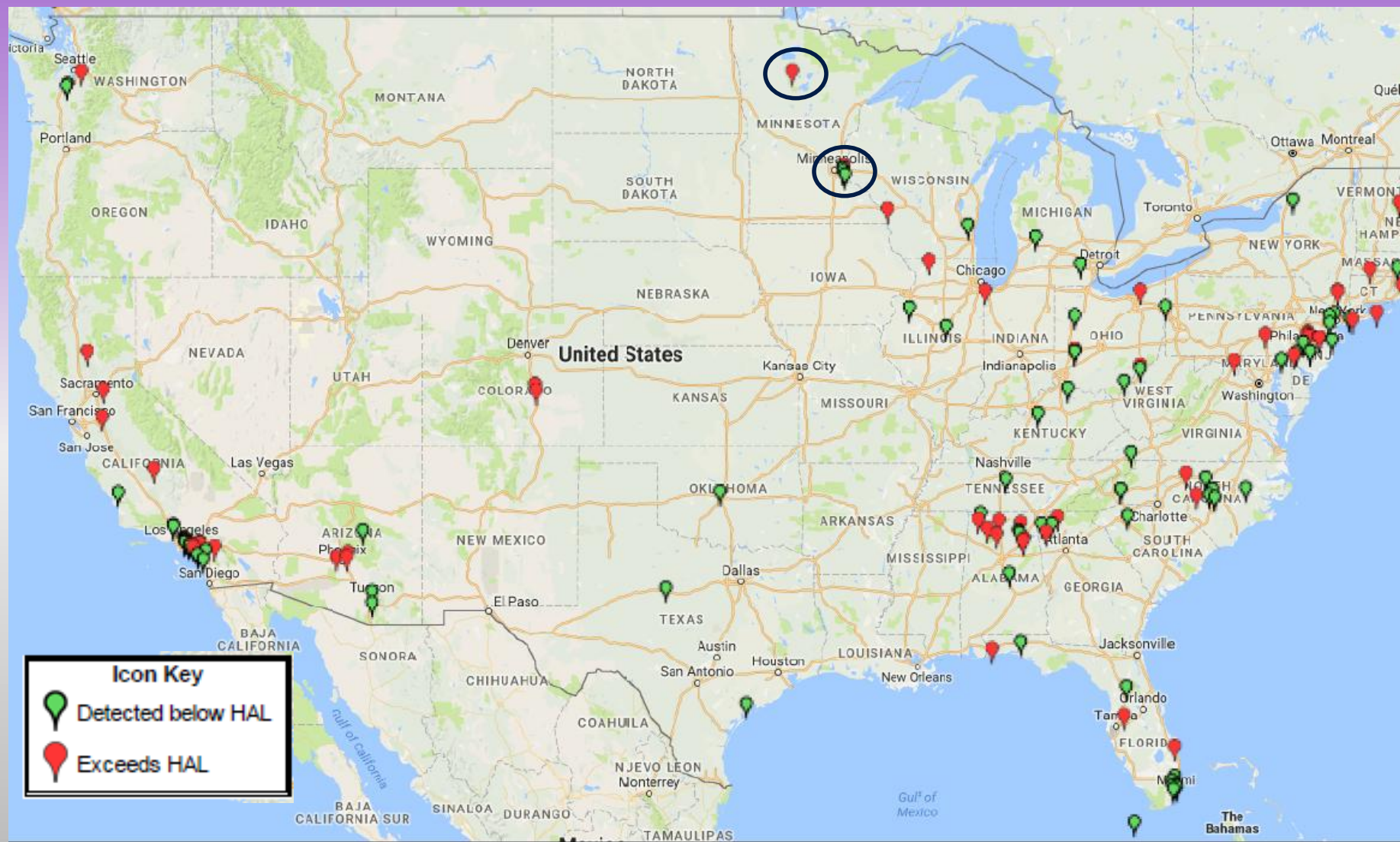


Figure from Andy Eaton, Eurofins – Eaton Analytical

PFASs In The News Again

- **EPA Lifetime Health Advisories (HAs)**

- PFOS and PFOA – 70 ng/L, individually or combined
- Based on animal studies and human correlation studies suggesting developmental & immune system effects
- Short-term exposure concerns for developing fetuses, infants, and children

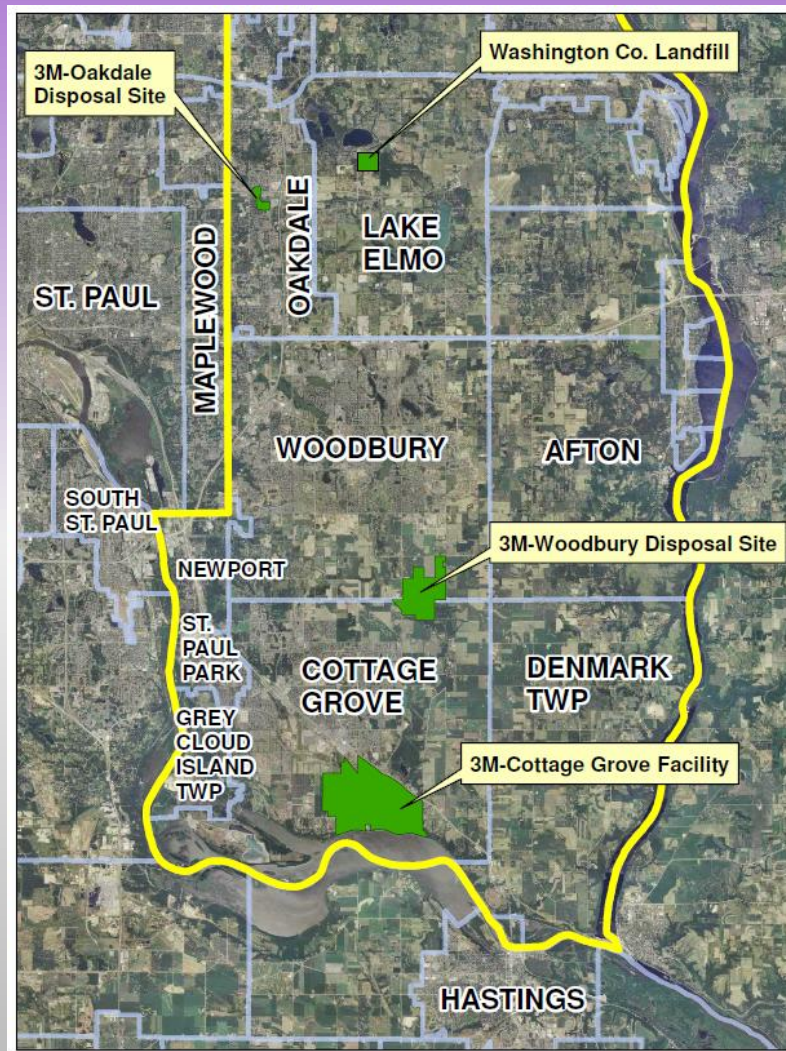


- **MDH Evaluation**

- Currently using EPA HAs for PFOS and PFOA
- Calculating additivity using PFBA and PFBS HRLs (7 ug/L) and surrogate value for PFHxS (70 ng/L)
- Hope to establish new HBVs in early 2017
- Values may be lower than EPA HAs

PFASs in the East Metro

- Manufactured in Cottage Grove, MN since the 1940s
- Wastes disposed of at plant and 3 major off-site disposal areas
- Investigated since 2003
- New EPA Health Advisories for PFOS & PFOA: more sampling & well advisories

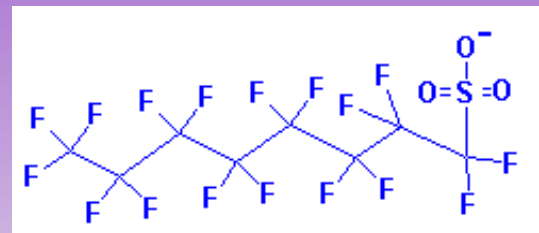


Location of 3M PFC Sites in Washington Co., Minnesota

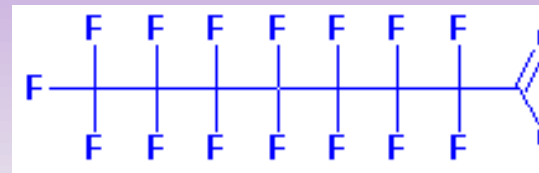


PFCs of Concern in Washington Co.

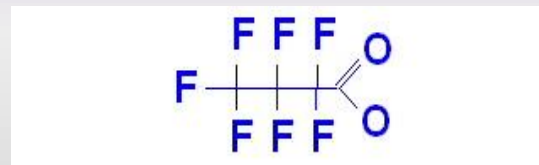
- **PFOS: $C_8F_{17}SO_3^-$**
Perfluorooctane sulfonate



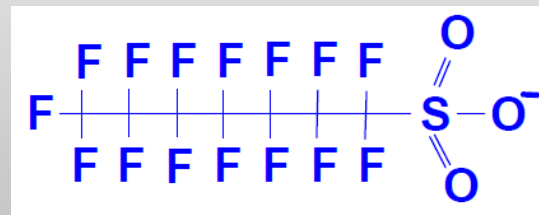
- **PFOA: $C_8F_{15}O_2^-$**
Perfluorooctanoic acid



- **PFBA: $C_4F_7O_2^-$**
Perfluorobutanoic acid



- **PFHxS: $C_{10}F_{19}SO_3^-$**
Perfluorohexane sulfonate



Other PFCs detected: PFPeA, PFHxA, PFBS

Bedrock Structures & Groundwater

• Faults

- NE-SW trending block faults; up to 150 ft. displacement
- Associated joint sets

• Fractures (syst. & non-syst.)

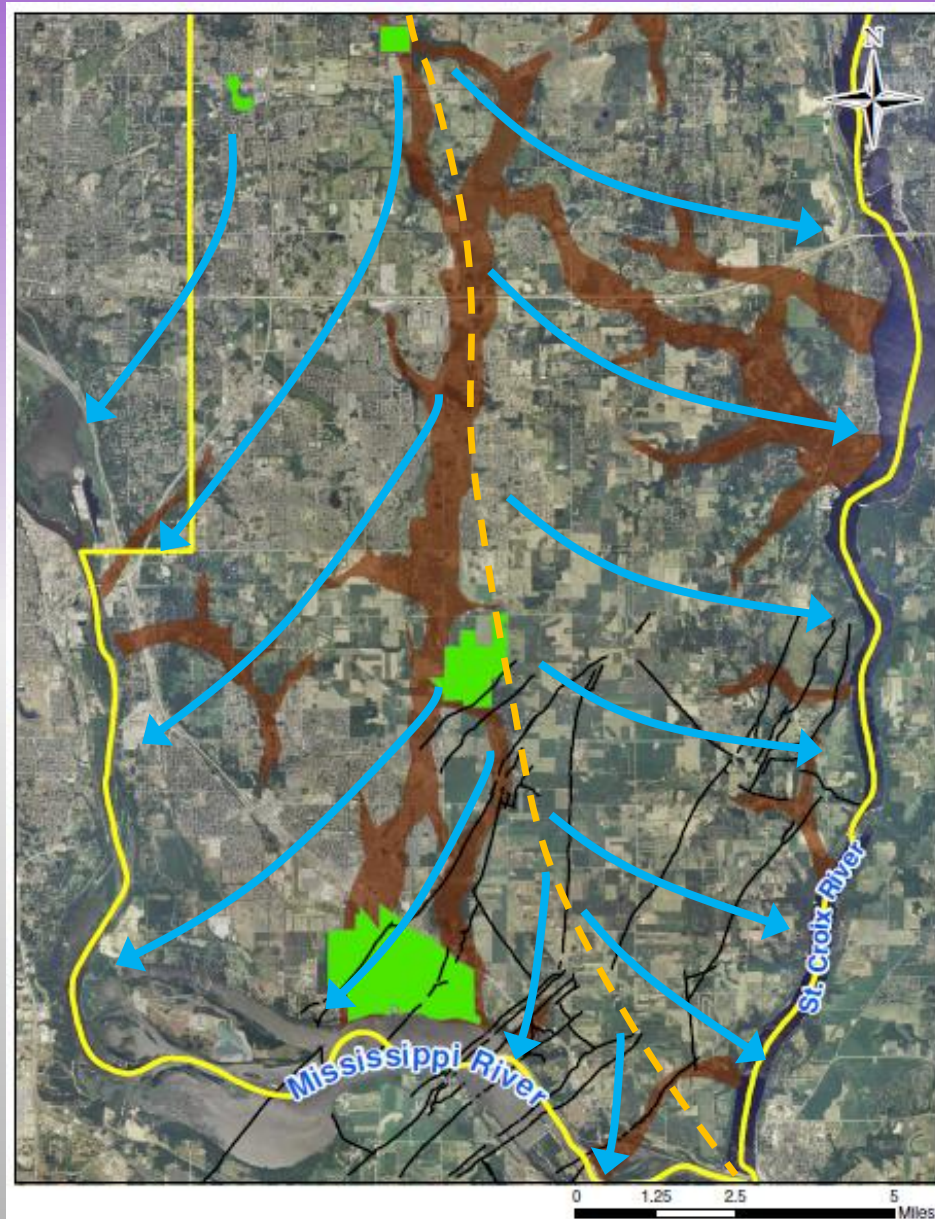
- Perpendicular and parallel to bedding
- Karsted, esp. Prairie du Chien

• Buried Bedrock Valleys

- Associated karst
- Conduits to St. Peter, Prairie du Chien & Jordan aquifers

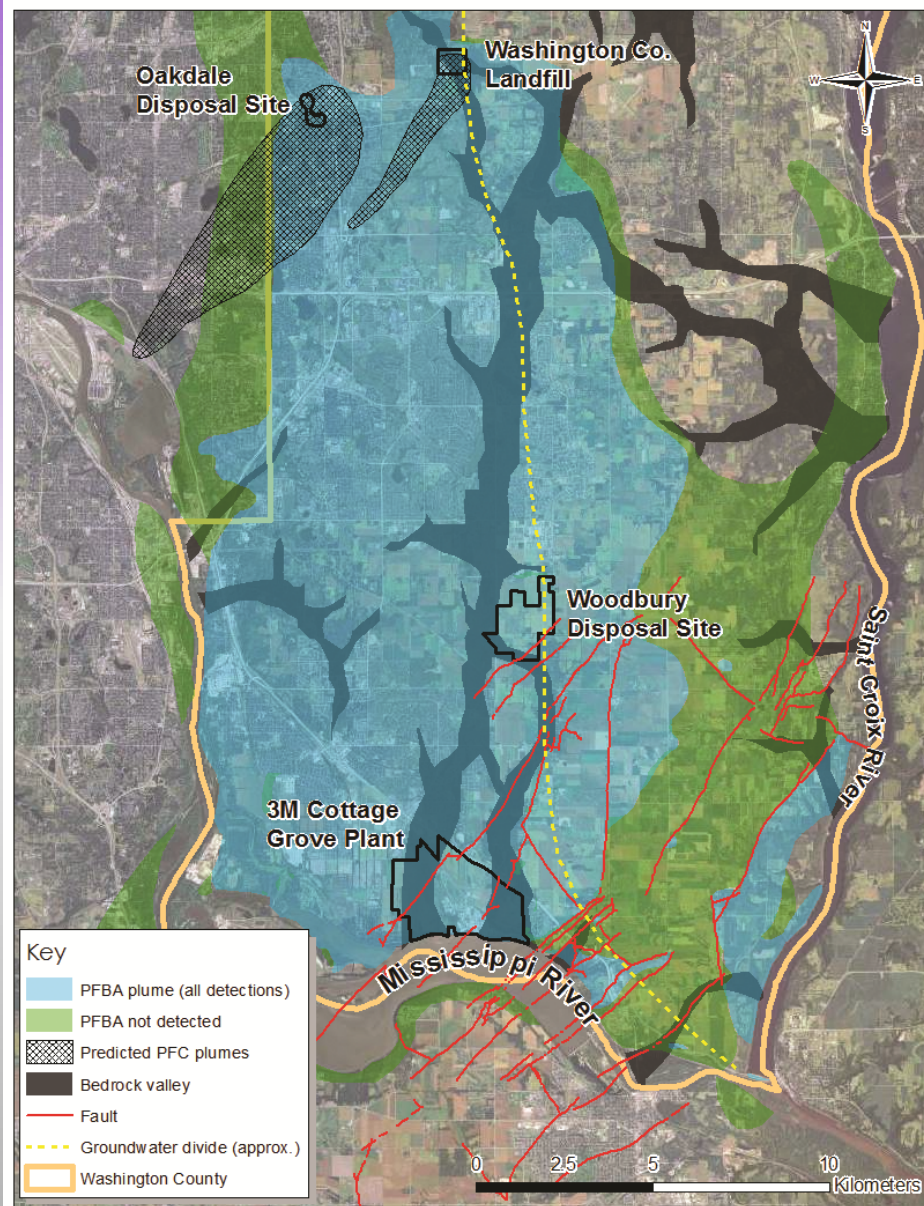
• Groundwater Divide

- Bisects south Washington Co.



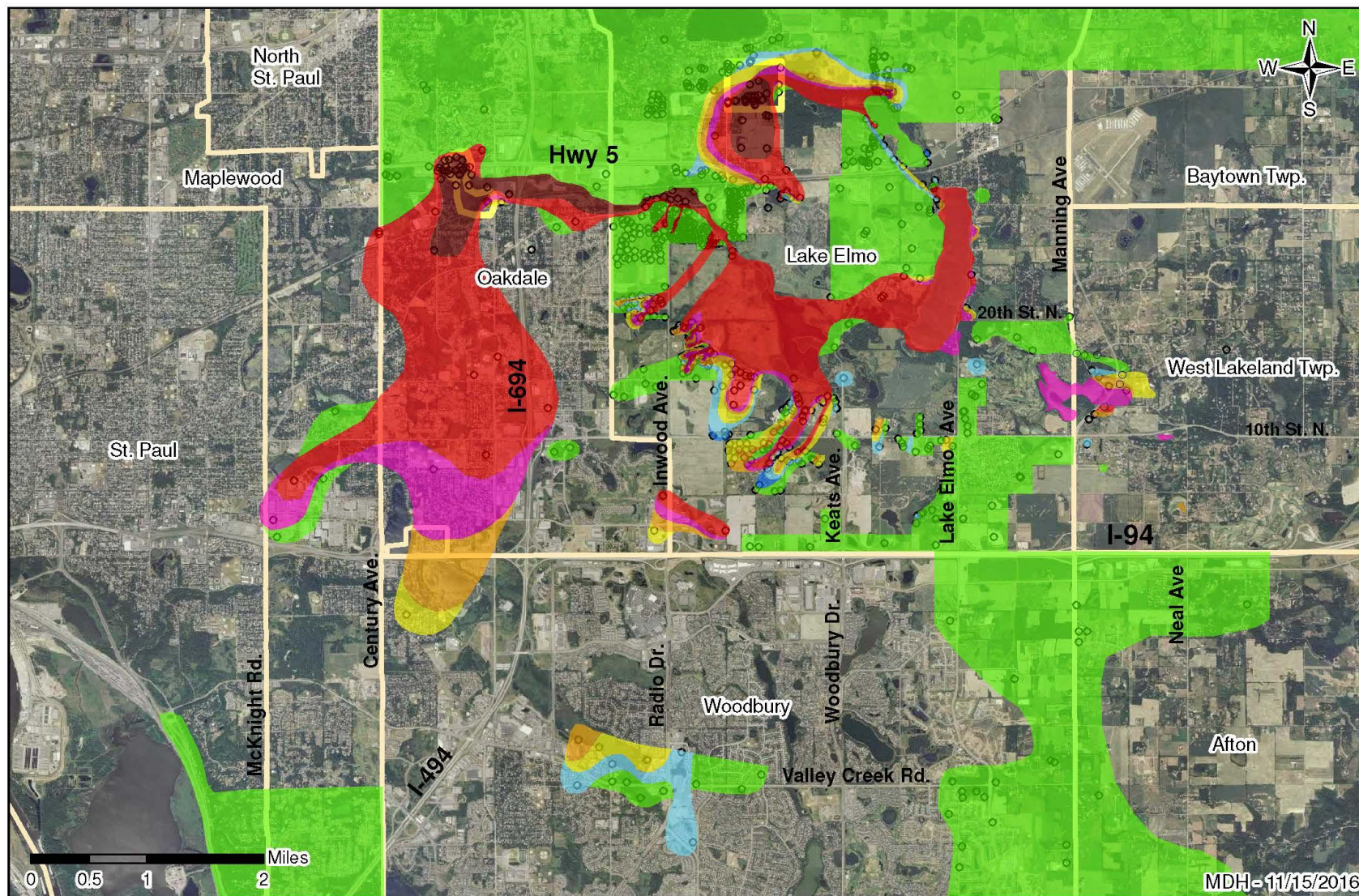
Result: A PFAS Megaplume

- **Over 100 mi² contaminated**
 - 4 major aquifers
 - 8 municipal systems
 - >1,500 private wells
 - Much larger plume than models predicted
- **PFBA most widespread**
 - Short-chain carboxylate
- **Distribution controlled by:**
 - Bedrock features
 - GW-SW interactions
 - Human interventions
 - PFC partitioning



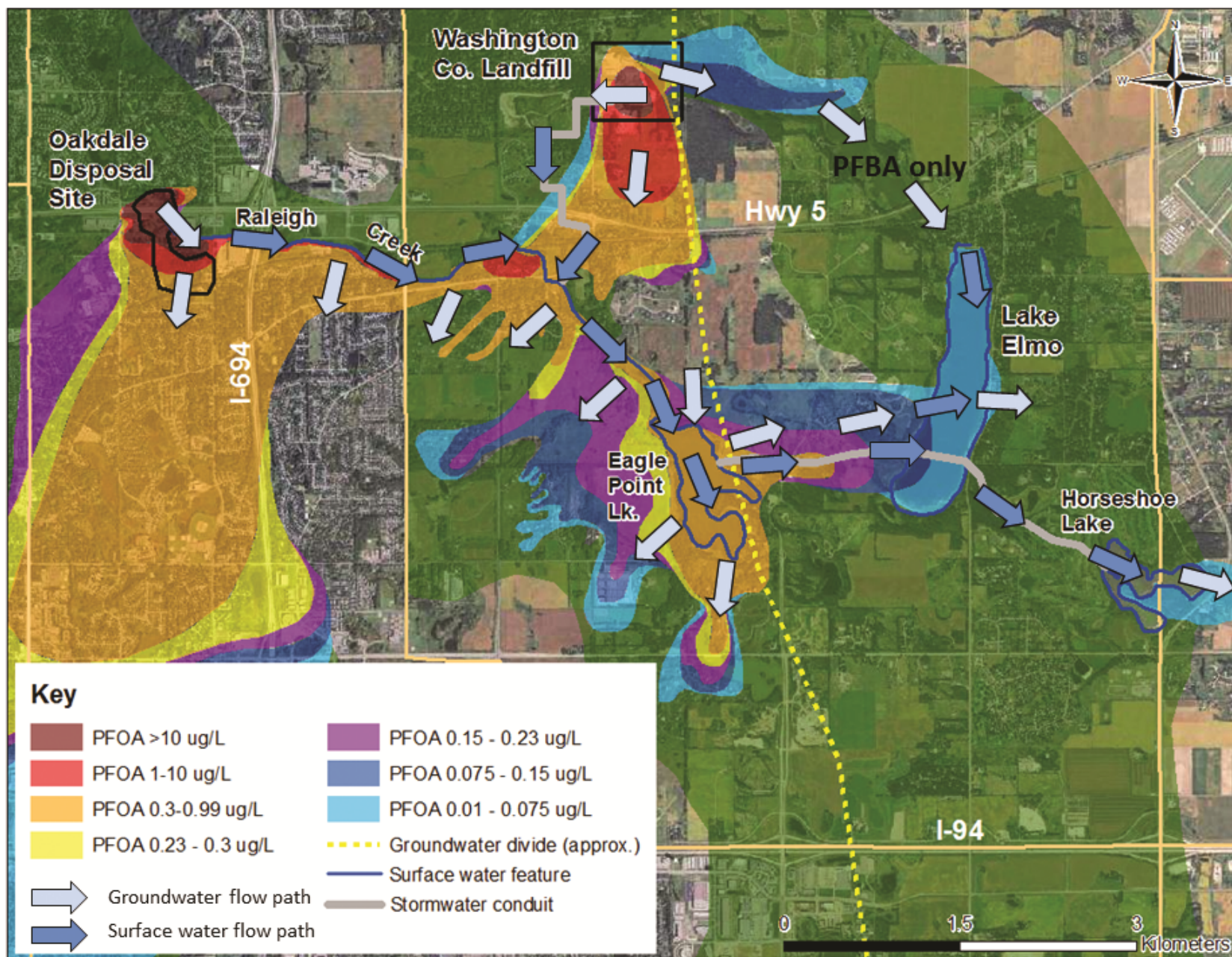
MPCA & MDH Response to EPA HAs

- **Expanded investigations in East Metro**
 - **West Lakeland Twp. now within affected area**
 - **Sampling 500+ wells this fall/winter**
 - **Surface water transport again a major pathway**
- **140+ new well advisories issued (so far)**
- **Bottled water → GAC or city water**
- **Working w/ affected public water systems (Oakdale, Bemidji, Cottage Grove)**
- **MN Public Health Laboratory lowered PFC reporting limits**

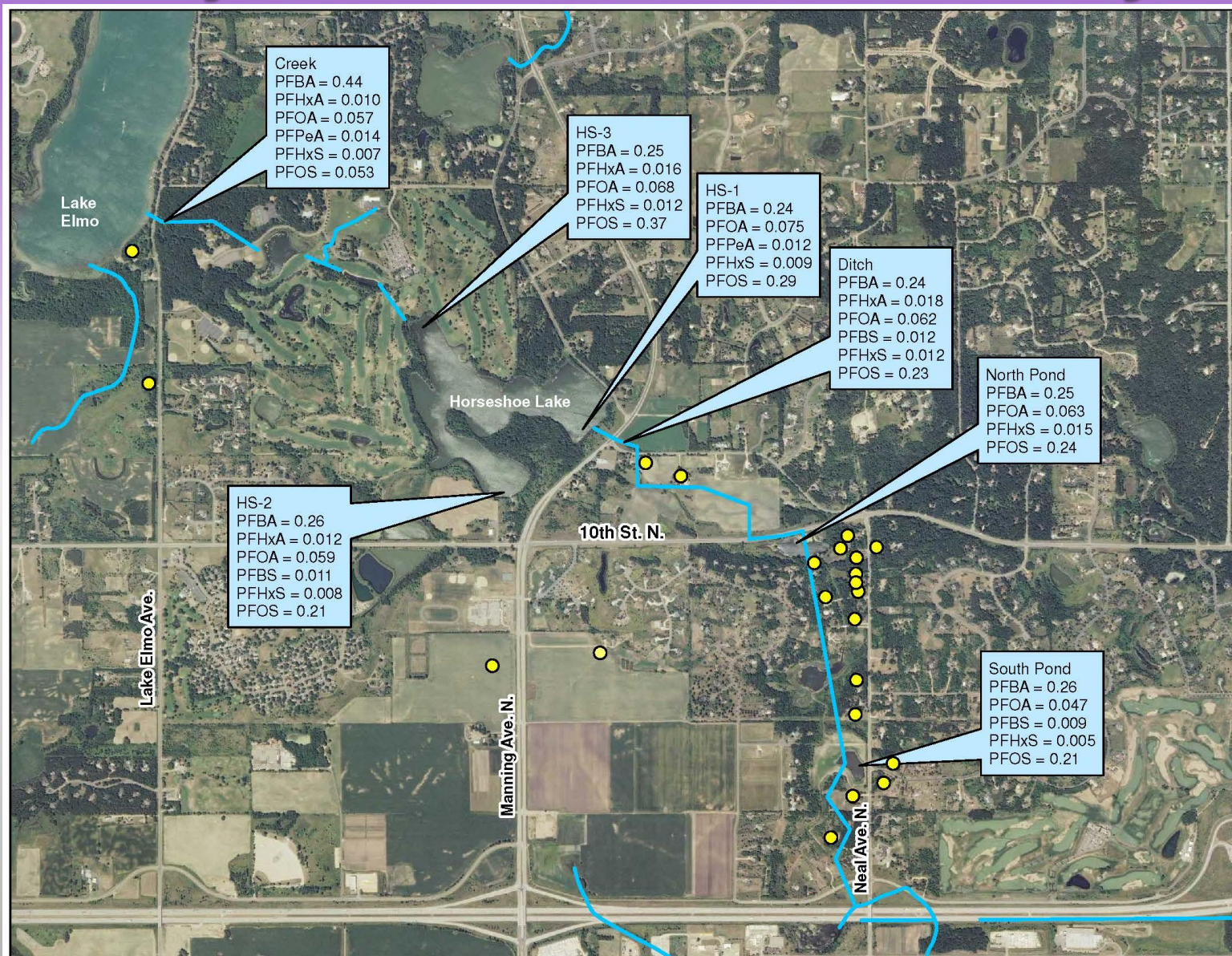


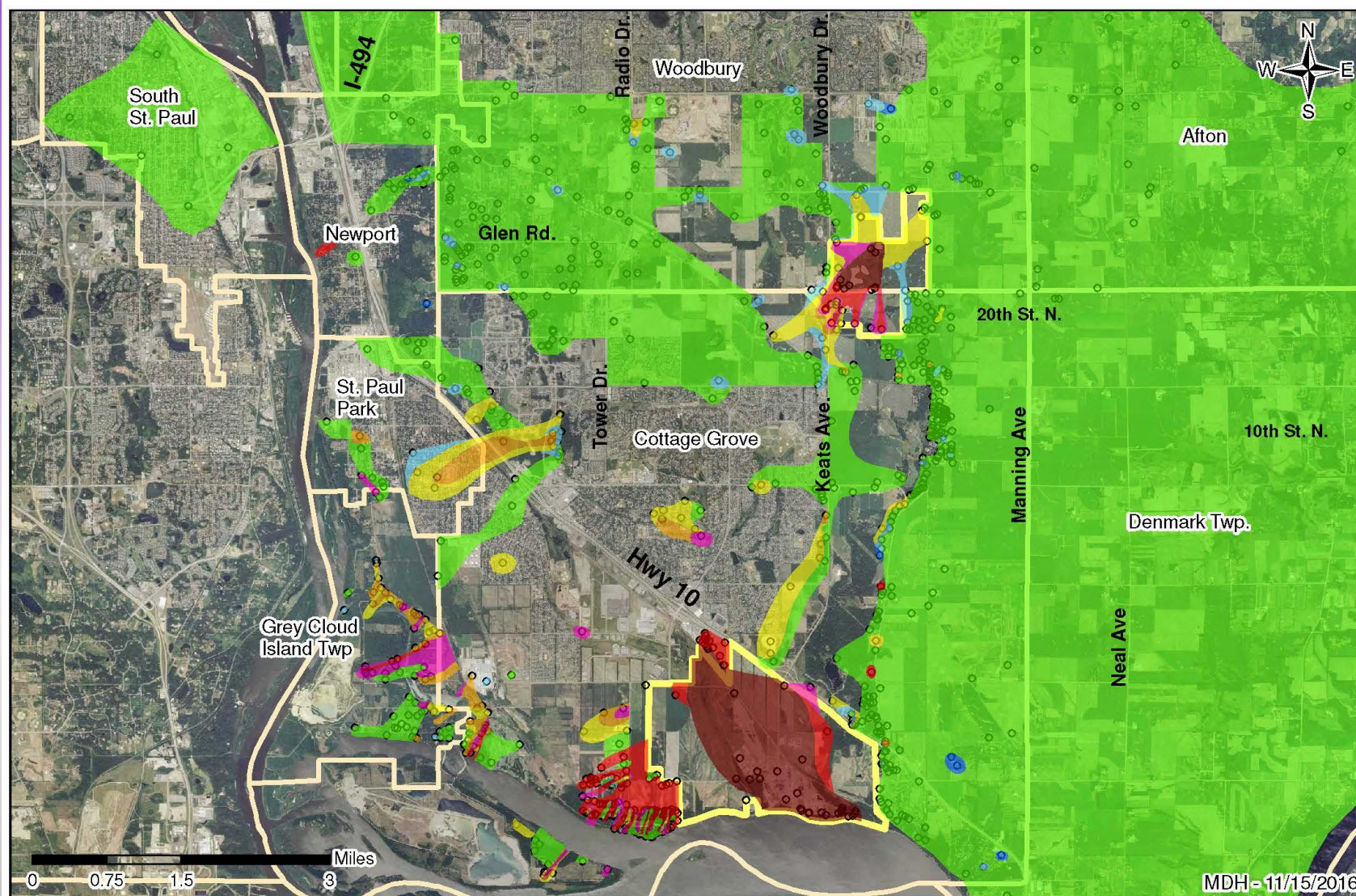
PFOA in Washington County Groundwater - All Aquifers - North



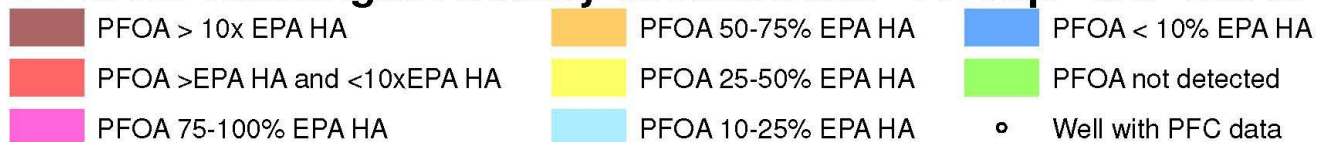


Project 1007: The Rest of the Story





PFOA in Washington County Groundwater - All Aquifers -South



Source Area Cleanup Actions

• Washington County Landfill

- 2 M yd³ waste excavated, placed in containment cells

• 3M-Oakdale

- Soil vapor extraction
- Excavated ~27,000 yd³ soil
- Groundwater extraction system upgraded, GAC treatment added



• 3M-Woodbury

- Excavated ~30,000 yd³ soil
- Evaluating pumping rate reductions



• 3M-Cottage Grove

- Excavated ~60,000 yd³ soil; dredged ~12,000 yd³ sediment
- Groundwater extraction & treatment systems upgraded

Drinking Water Treatment

• Public Wells

- Oakdale
 - 5 and 9 – large scale GAC
 - New advisories for wells 1, 2, 7, and 8
- Other East Metro cities
 - MDH monitors regularly
 - Some wells may exceed additivity evaluation once new HBVs set



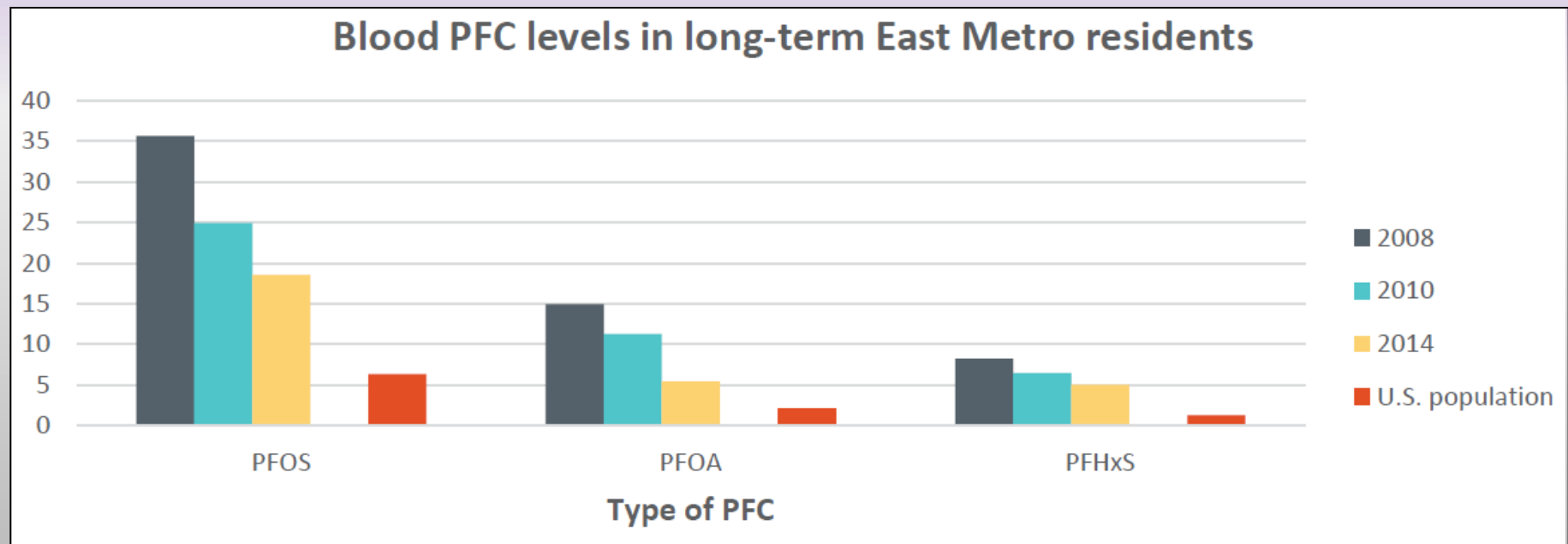
• Private Wells

- 1,500+ sampled to date
- Approximately 500 sampled annually
- 320+ well advisories have been issued since 2005
- Residents provided bottled water, then GAC
- 220 homes in Lake Elmo connected to city water (2007)



Biomonitoring

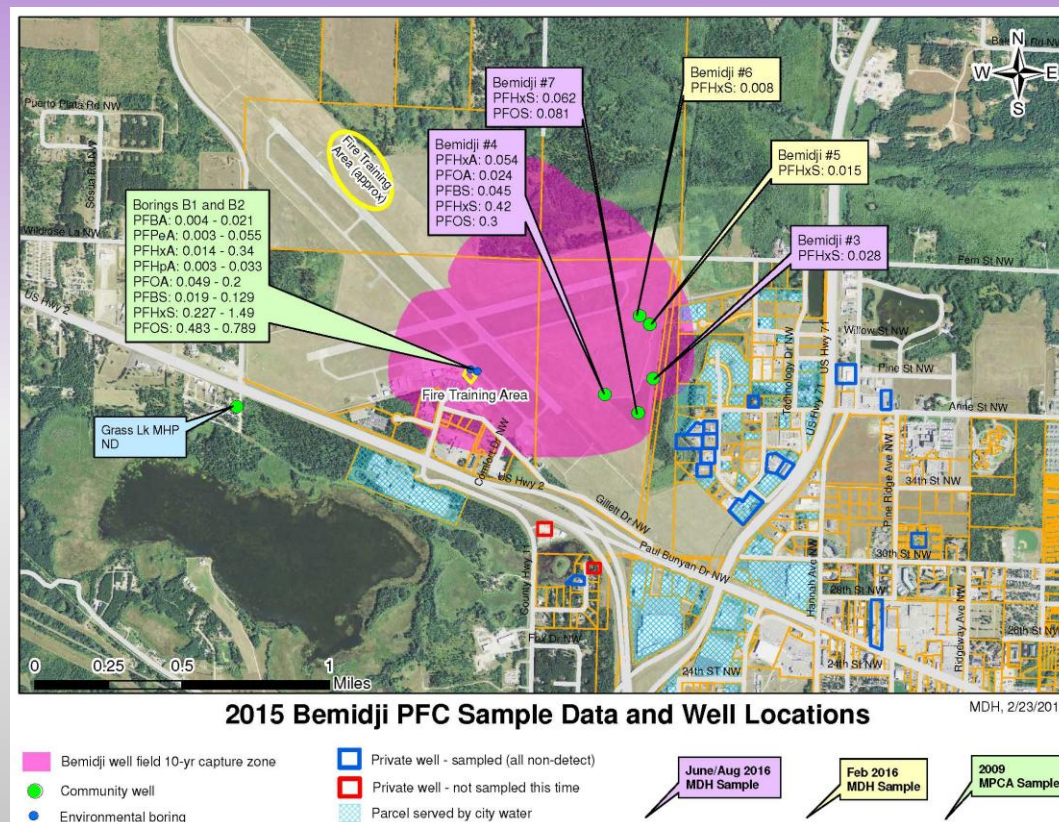
- Three rounds: 2008, 2010, 2014
- 196 initial participants (164 returned)
- PFCs decreased in blood of people drinking treated water (but ave. concentrations > national ave.)



Concentrations in micrograms PFC in liter blood (ppb)

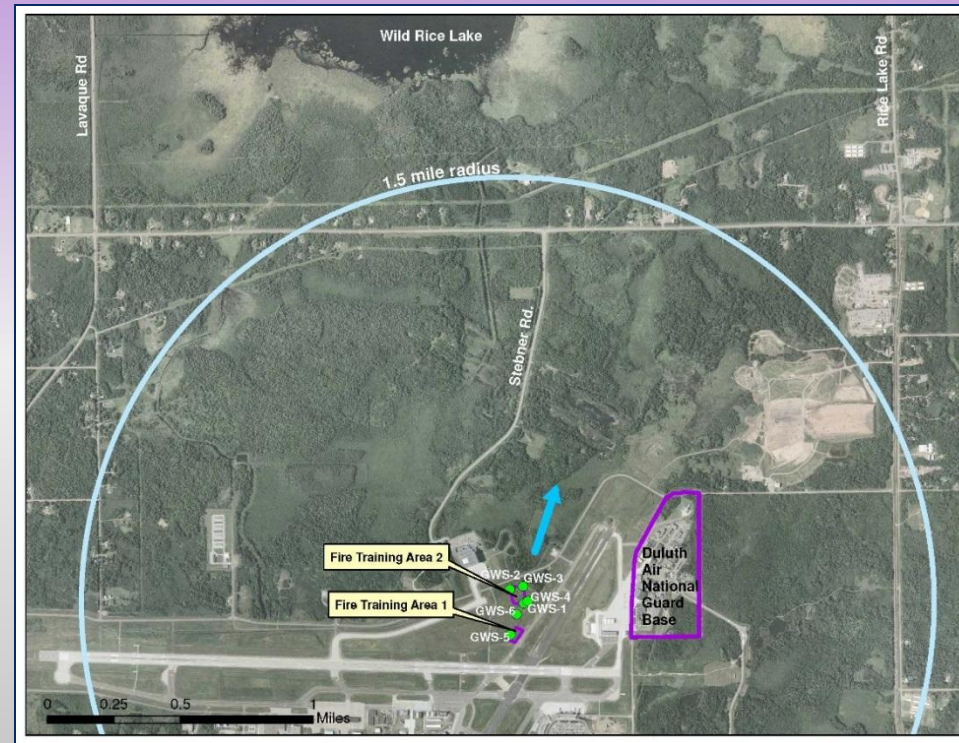
Bemidji Airport Site

- **AFFF Site (2008-2009)**
 - Investigated by MPCA & MDH
 - Low levels in city wells
 - Mainly PFHxS, PFOS, PFBS
 - Trace PFBA in private wells
- **UCMR3 (2014)**
 - Lower MDLs = more PFCs
 - Concentrations increasing
- **MDH (2015-2016)**
 - Two city wells exceed HAs
 - Assisting city w/ well mgmt.
 - Private well monitoring (ND-trace PFBA)
- **Additional investigations planned (2017)**



Duluth Air National Guard Base

- **AFFF Site (2010)**
 - Investigated by MPCA & DOD
 - Two training areas
 - Seven PFASs in groundwater:
 - PFHxA, PFPeA, PFOA, PFHxS dominate the signature
 - Trace PFHxS, PFHxA, PFOA, and PFOS in a few private wells
 - On-going site characterization and remedial design
- **EPA Health Advisories**
 - Additional private well testing will be needed



ITRC PFAS Team

- **Interstate Technology and Regulatory Council**

- A program of the Environmental Council of the States (ECOS)
- State-led organization to advance innovative environmental decision making
- Guidance documents & training courses

- **PFAS Team**

- Starting in January 2017
- Develop PFAS factsheets & internet based modular training:
 - History, use, and environmental sources
 - Nomenclature and physicochemical properties
 - Fate & transport
 - Site characterization tools, sampling techniques, and analytical methods
 - Remediation technologies & methods
 - Regulatory summary
 - Technical challenges & uncertainties

ITRC PFAS Team

- **For more information:**

- www.itrcweb.org
- Rebecca Higgins, MPCA
 - 651-757-2240
 - Rebecca.Higgins@state.mn.us

Acknowledgements

- **MDH – Environmental Health Division**
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- **West Central Environmental Consultants (WCEC)**
- **Interpoll Laboratories**
- **Minnesota Geological Survey**
- **Washington County**
- **Cities of Oakdale, Lake Elmo, Woodbury, Cottage Grove**
- **Valley Creek Watershed District**
- **3M Company**
- **Weston Solutions**
- **Barr Engineering**
- **Agency for Toxic Substances & Disease Registry (ATSDR)**
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The opinions expressed are those of the author and do not necessarily reflect the official views of ATSDR, the CDC, the Department of Health and Human Services, or the Minnesota Department of Health.

QUESTIONS?
