## DEPARTMENT OF HEALTH

### **PFAS in East Metro Water Supplies: A Long Story** 2019 Water Summit

James Kelly, M.S.

Manager, Environmental Surveillance & Assessment

**Environmental Health Division** 

#### DEPARTMENT OF HEALTH

No matter who or where you are in Minnesota



MDH Environmental Health Division works behind the scenes to create conditions that support the health of all Minnesotans.



#### The MDH Mission - Protecting, maintaining, and improving the health of all Minnesotans.

# What Are Per- and Polyfluoroalkyl Substances (PFAS)?

- Large (4,000+) class of surfactants with unique chemical & physical properties that make many of them extremely persistent and mobile in the environment
- Used since 1940s in wide range of consumer and industrial applications



## **Basic PFAA Structure**

### Perfluoroalkyl Acids (PFAAs)

- Fully (per-) fluorinated chain (2 to 40+ carbon "tail")
- Functional group ("head")
  - PFCAs: Carboxylate group (COO<sup>-</sup>)
  - PFSAs: Sulfonate group (SO<sub>3</sub>-)





Source: ITRC Naming Conventions and Physical Chemical Properties factsheet

## **Highlights of PFAA Properties**

#### • C-F is the shortest and strongest bond in chemistry

- Small, highly electronegative fluorine atoms "shield" the carbon from chemical reactions
- No biological or chemical degradation of PFAAs under natural conditions
- PFAAs thermally degrade only at high temperatures

#### • Perfluoroalkyl acids (PFAAs) are negatively charged

- Present as anions in the environment
- Interact and sorb onto positively charged minerals
- Controlled by pH, chain length, and functional ("head") group



Source: open access image - bing.com

#### High C-F Bond Energy

kJ/mol of bonds				
C-F	485			
C-H	436			
C-C	346			
C-CI	339			
C-N	305			
C-Br	285			
C-S	272			

## **Highlights of PFAA Fate & Transport**

### • PFAAs generally have low volatility



- People generally not exposed by inhalation
- Don't have to worry about vapor intrusion at most sites
- Air transport may occur for PFAAs sorbed to particulates or dissolved in water droplets
- Many precursors are volatile and some may degrade to PFAAs
- PFAAs not well absorbed through skin 😬
- PFAA movement in the environment has some predictability
  - Controlled largely by chain-length and functional group
  - Implications for removing them from the environment





## "What's So Special About PFAS?"

#### Table modified from Ducatman, 2018

	PFAAs	Dioxins & PCBs
Highly water soluble	Yes	No
Bind well to soil & sediments	Νο	Yes
Degrades to some extent in the environment	Νο	Yes
Bioaccumulate in fish Complicates our	Yes*	Yes
Bioaccumulate in lipids understanding of bioaccumulation ppt in water	Νο	Yes
"Proteinphilic" and toxicity ppb in serum	Yes	Νο
Drinking water is major exposure route	Yes	No

\* True for PFAAs with 8 or more fluorinated carbons (PFOS, PFNA, and longer-chain)

## **PFAS: A Classic Emerging Contaminant Challenge**

#### Widely present in the environment

• Detected in drinking water and biota; other media

#### Evolving understanding of fate & transport

 New pathways and affected areas create sense the problem is "getting worse"

#### • Evolving analytical capabilities

 Expanding analyte lists and lower detection limits = "more detections" and sense the problem is "getting worse"

#### Limited remedial technology options

- Evolving risk assessment
  - Changing/differing guidance values = public confusion and sense the problem is "getting worse"

### Risk Communication



### The Science of PFAS Toxicology

- A relatively young science (early 2000s)
- Active area of scientific research (75+ papers per month)
- Many key questions yet to be answered
- Curious differences between sexes and species
- Stability and persistence in the environment/body, water solubility make them unique

### Overview of PFAS Health Effects: What do we know?

- Laboratory Animal Studies (experimental, causal)
  - Developmental Effects (e.g., ↓ body weight, delayed puberty & mammary gland development \_ accelerated puberty \_, changes in lipid metabolism & liver histology)
  - Endocrine (e.g.,  $\downarrow$  thyroid hormones)
  - Immune (e.g.,  $\downarrow$  immune response,  $\downarrow$  spleen & thymus weight)
  - Kidney (e.g., ↑ organ weight)
  - Liver (e.g.,  $\downarrow$  cholesterol,  $\uparrow$  organ weight, evidence of cellular damage)
  - Cancer?
- Based on multiple animal species (rats, mice, monkeys, etc)
- Carefully controlled to evaluate effects of PFAS only
- Often conducted by industry scientists
- Not all studies look at all types of effects
- Often study single chemicals, not mixtures



### Overview of PFAS Health Effects: What do we know?

- Human Epidemiology Studies (associations, not causal)
  - Developmental (e.g.,  $\downarrow$  birth weight)
  - Endocrine (e.g., thyroid hormone levels)
  - Immune (e.g.,  $\downarrow$  vaccine response, ulcerative colitis)
  - Kidney (e.g., 个 uric acid)
  - Liver (e.g., ↑ serum lipids and liver enzymes)
  - Cancer (e.g., testicular, kidney)



- Largest was the C8 Study in Ohio/West Virginia, over 60,000 people
- Found "probably links" (legal term) between PFAS exposure and several health conditions
- Often have trouble determining exposure history
- Difficult to evaluate mixtures of PFAS
- EPA/CDC/ATSDR will be leading additional studies in PFAS exposed communities in coming years

### Setting MDH Health-Based Values for Water



## MDH – Standard Water Guidance

### Standard Health-Based Guidance (HBG) is based on:

- Reference Dose (RfD) represents a dose at which there is little or no risk of health effects (for PFOA and PFOS this dose is best represented by a serum concentration)
- Water Intake Rate how much water someone drinks perday on operating dy weight basis. Chronic intake rates typically used.
- Relative source contribution (RSC) Multiple sources of examples exposure only come from water so that total exposure does

## Additional Exposure Concerns

- Impact of Bioaccumulation Potential
  - Long half-life results in exposures, even short duration, to stay in body for years beyond period of external exposure
  - Repeated exposures lead to accumulation (build-up) within the body
  - Water concentrations in ppt result in serum concentrations in ppb
  - Accumulated levels can be transferred to offspring
    - Placental transfer and Breastmilk transfer





Much higher fluid intake rates in infants & young children

## PFAS Water Guidance Health Endpoints

PFAS	Health Endpoints <sup>1</sup>	Mean Human Half-life <sup>2</sup> (~5 – 95 <sup>th</sup> percentile range)
<u>PFBA</u>	Liver, Thyroid	3 days (1.2 – 4.6 days)
<u>PFBS</u>	Developmental, Female Repro system, Thyroid	27.7 days (13.1 – 45.7 days)
PFHxS	Liver, Thyroid	5.3 years (2.2 – 14.6 years)
<b>PFOA</b>	Developmental, Immune, Liver, Kidney	2.3 years (1.5 – 7.0 years)
<u>PFOS</u>	Developmental, Immune, Liver, Thyroid, Adrenal	3.4 years (2.2 – 8.5 years)

<sup>1</sup>Used in additivity (mixtures) assessments <sup>2</sup>Extreme values removed

More information can be found at: <u>http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html</u>

## **How PFAS Water Guidance has Changed**

- MDH health-based guidance values evolve over time as additional research becomes available
- Surrogate values used when widespread detection of chemical in drinking water, but insufficient toxicological data to set an HBV
- Health Risk Index (HI): allows MDH to evaluate mixtures of similar chemicals
  - Similar to TEQ approach
  - If HI > 1, considered an exceedance

	PFOA	PFOS	PFBA	PFBS	PFHxS
2002	7	1			
2006	1	0.6	1		
2007	0.5	0.3	7		
2009	0.3	0.3	7	7	
2013	0.3	0.3	7	7	0.3
2016	0.07	0.07	7	7	0.07
2017	0.035	0.027	7	3/2	0.027
2019	0.035	0.015	7	3/2	0.047

Blue = HRL; Red = HBV; Green = Surrogate

$$H = \underline{PFOA}_{[conc]} + \underline{PFOS}_{[conc]} + \underline{PFBA}_{[conc]} + \underline{PFBS}_{[conc]} + \underline{PFHxS}_{[conc]}$$

$$0.035 \quad 0.027 \quad 7 \quad 3 \quad 0.027$$

16

### **MDH Guidance Summary**

- Based on protection of susceptible & highly exposed populations
- Protective for tap water used for drinking, cooking, showering, and other uses
- Cumulative additivity assessment of chemicals with similar health endpoints

Breastfeeding can be a significant exposure pathway for PFHxS, PFOS, and PFOA. However, breastfeeding is important for the short and long term health of both a mother and infant. MDH recommends that women currently breastfeeding, and pregnant women who plan to breastfeed, continue to do so.



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



### **Groundwater Flow**

- A groundwater divide extends from north to south beneath the county
- East of the divide groundwater flows to the St. Croix River
- West of the divide groundwater flows to the Mississippi River
- Close to where the two rivers meet, the flow "fans out" toward either river
- Locally, groundwater flow may be influenced by pumping wells



### East Metro PFAS "Mega-Plume"

- Over 150 sq. mi.
  - 4 major aquifers
  - 8 municipal systems (140,000+ users)
  - Thousands of private wells
  - Several area lakes & streams
    - Fish consumption advisories (esp. Lake Elmo)

#### PFBA most widespread

- High levels of PFBA in source areas
- More mobile

# • PFOS and PFOA driving drinking water advisories



## PFAS in groundwater – Washington County, MN

- PFAAs highly soluble, mobile, persistent = very large plumes
  - Much larger than predicted by models
  - Co-mingled plumes
- PFBA most widespread
  - Extremely soluble and mobile = groundwater tracer
  - Distal plume difficult to distinguish from "ambient" levels
- Distribution controlled by:
  - Bedrock features (buried valleys and faults —)
  - Groundwater divide (Mississippi R. and St. Croix R. - -)
  - Groundwater surface water interactions
  - PFAS chemical properties (partitioning)
  - Source area PFAS "signature"
  - Groundwater pumping



NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data; PFBA HRL = 7 ppb 3/26/2018

#### 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.



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

### Well sampling effort & drinking water advisories

- ~3,000 wells sampled since 2003
  - Frequent, intensive monitoring of private wells:
    - Near source areas
    - Areas with high or changing PFAS concentrations
    - Areas with complex geology
  - Less frequent monitoring of "sentry" private wells:
    - Areas with low and stable PFAS concentrations
    - Areas with relatively simple geology
- ~ 1,100+ drinking water advisories issued



## Municipal Well PFAS Impacts

- MDH Advisories issued to Cities of Oakdale, Cottage Grove, Lake Elmo, St. Paul Park and Woodbury
- Oakdale Carbon Treatment funded by 3M prior to 2007 Consent Order
  - 7 of 9 wells exceed MDH guidance
- Cottage Grove "Temporary" Carbon Treatment for 2 wells
  - 8 of 12 wells exceed MDH guidance (water restrictions summer 2017)
- Lake Elmo Discontinued use of Well #1 (one of three wells)
  - 3M funded connection of ~200 homes to municipal supply prior to CO
- St. Paul Park Discontinue use, one of three Wells
  - Temporary treatment planned for 2 wells
- Woodbury Five of 19 wells impacted

### **Drinking Water Response Actions – East Metro**

#### GAC treatment where HRLs/HBVs exceeded





### East Metro PFAS Biomonitoring Projects

- Directed by Minnesota Legislature in 2007 to test blood levels in East Metro communities (MN Statutes 144.995-144.998)
- Focused on adults in 2 communities: municipal water and private well users
- Studies in 2008, 2010, 2014
- Questions addressed
  - Are residents in affected communities having unusual PFAS exposures?
  - Have efforts to reduce drinking water exposure to PFAS worked?
  - Do other factors (such as diet, consumer products, occupation) help explain PFAS levels?

### How biomonitoring studies worked

- Participants randomly selected
  - Water utility billing records
  - Lists of people with contaminated private wells
- Contacted participants by mail, asked for informed consent, sent questionnaire
- Gave blood sample at local health clinics
- MDH Public Health Laboratory analyzed blood samples for 7-8 PFAS
- Returned individual and group results to participants

(Landsteiner et al., 2014, Journal of Environmental Health, v. 77)



### PFAS blood levels in long-term East Metro Residents (n=149)



### PFAS in New Oakdale Residents (2014, n=156)



## **Responding to Community Concerns**

- Water Filtration Testing
  - Very little information at first
  - Laboratory and field testing confirmed viability of GAC, reverse osmosis, and small consumer units
- Garden Produce Study
  - Identified uptake of PFAS in produce grown in gardens irrigated with PFAS contaminated water
  - Primarily PFBA
  - Below levels of health concern
    - (Scher et al., 2018, Chemosphere, v. 196)









### 2018 Health Outcomes Data Reports

#### DEPARTMENT OF HEALTH

#### East metro birth outcomes

LOW BIRTH WEIGHT AND PREMATURITY IN WASHINGTON AND DAKOTA COUNTIES (2000-2015)

This report responds to concerns in east metro communities around legacy perfluorochemicals (PFCs) contamination and adverse birth outcomes. MDH examined vital records data for two key indicators: low birth weight and prematurity. We looked at community-level trends to identify areas with unusually high rates of these indicators. Specifically we looked at whether these trends show differences related to social and economic factors that are important in identifying communities where people don't have what they need to be healthy.

#### **Key findings**

- There is a lot of variation but the small differences are not outside of what we would
  expect given what we know about the east metro and the rest of the state.
- Variation across areas and differences over time do not suggest any unusual increase in low birth weight or premature births in east metro communities.
- Health inequities across the diverse population are consistent with differences and trends we see across Minnesota. Addressing these inequities is a central piece of the department of health's work and priorities.

#### Figure 1

Cancer Incidence Rates Among Washington County Residents Compared to the Statewide Rates, 1988-2012, Both Sexes



### Fish Consumption Advice – Data from MN Lakes





### Fish Consumption Advice

#### • Different exposure pattern

- Water
  - Daily exposure
  - Single source (mostly)
- Fish
  - Less frequent exposure
  - Variety of sources/levels
- Fatty acids/other constituents in fish may counteract some effects from PFOS including immune effects
- Risks and benefits must be balanced



### Conclusions

- PFAS will remain an active area of scientific research and we can expect new information and findings
- Response across programs, agencies, and jurisdictions is crucial and requires good coordination
- National study data will help future understanding; MDH will be applying to participate
- This will be a long-term issue in the East Metro
- MDH will continue to follow the science of PFAS carefully



# Questions?

James.Kelly@state.mn.us (651-201-4910)

Slide Sources: Helen Goeden, Ginny Yingling, Jessica Nelson, Pat McCann