

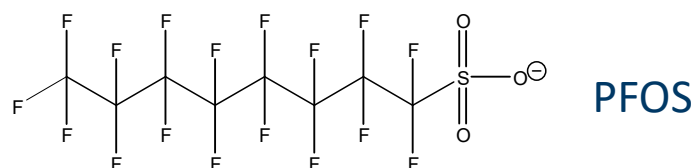
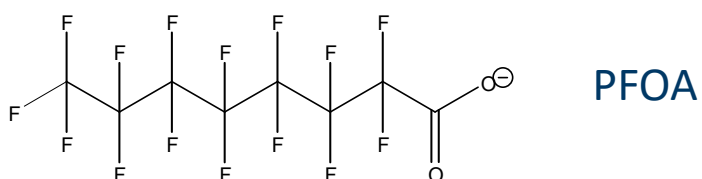


Environmental Testing, Biomonitoring and Partnerships: A Public Health Intervention Story to Address PFAS Groundwater Contamination in Minnesota

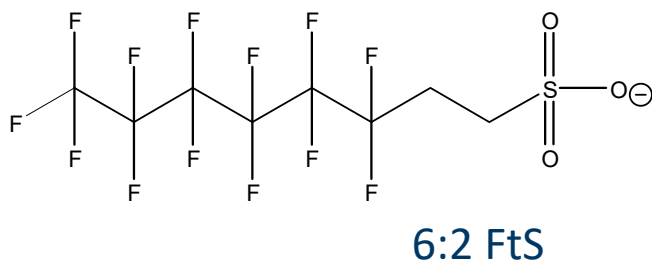
Carin Huset, PhD; Jessica Nelson, PhD; James Kelly, MS
Minnesota Department of Health
August 9, 2018

What are PFAS?

• Perfluoroalkyl substances



• Polyfluoroalkyl substances



Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

Non-Polymers

Perfluoroalkyl Substances

Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines

- (Aliphatic) perfluorocarbons (PFCs)
- Perfluoroalkyl acids
- Perfluoroalkane sulfonyl fluorides
- Perfluoroalkane sulfonamides
- Perfluoroalkyl iodides
- Perfluoroalkyl aldehydes

Polyfluoroalkyl Substances

Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines

- Perfluoroalkane sulfonamido derivatives
- Fluorotelomer-based compounds
- Semifluorinated *n*-alkanes and alkenes

Polymers

Fluoropolymers

Carbon-only polymer backbone with fluorines directly attached

Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers

Variable composition non-fluorinated polymer backbone with fluorinated side chains

- Fluorinated acrylate and methacrylate polymers
- Fluorinated urethane polymers
- Fluorinated oxetane polymers

Figure from Buck et al, IAEM, 2011

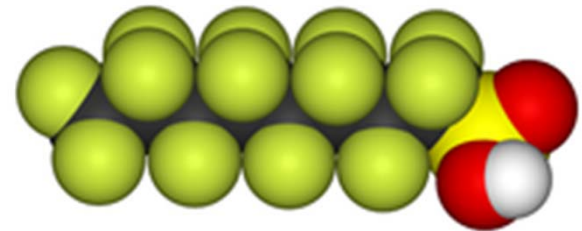
Why do we study PFAS?

- Persistent and do not biodegrade
- They are globally distributed
 - Found in air, water, sediments, wildlife & humans
- They bioaccumulate and biomagnify
 - Half-lives (human serum elimination)
 - PFOA 3.5 years
 - PFOS 4.8 years
 - PFHxS 7.3 years
- Toxicological effects not fully understood
 - PFOA probable carcinogen



Application and Use of PFAS

- Surfactant properties
- Strength of the C-F bond
- Commercial applications
 - Stain and water repellant coatings
 - Paper & packaging
 - Textiles & Carpets
 - Performance chemicals
 - Industrial surfactants
 - AFFF
 - Insecticides



Background - Why Are PFAS An Issue in MN?

- We are the home of 3M, originally known as Minnesota Mining and Manufacturing
- 3M operates a large chemical plant on the banks of the Mississippi River in Cottage Grove, Minnesota
- PFAS were manufactured at the plant for decades
- PFAS production wastes and wastewater treatment sludge was disposed of both on and off site; primary PFC waste disposal sites are located in Washington Co., Minnesota

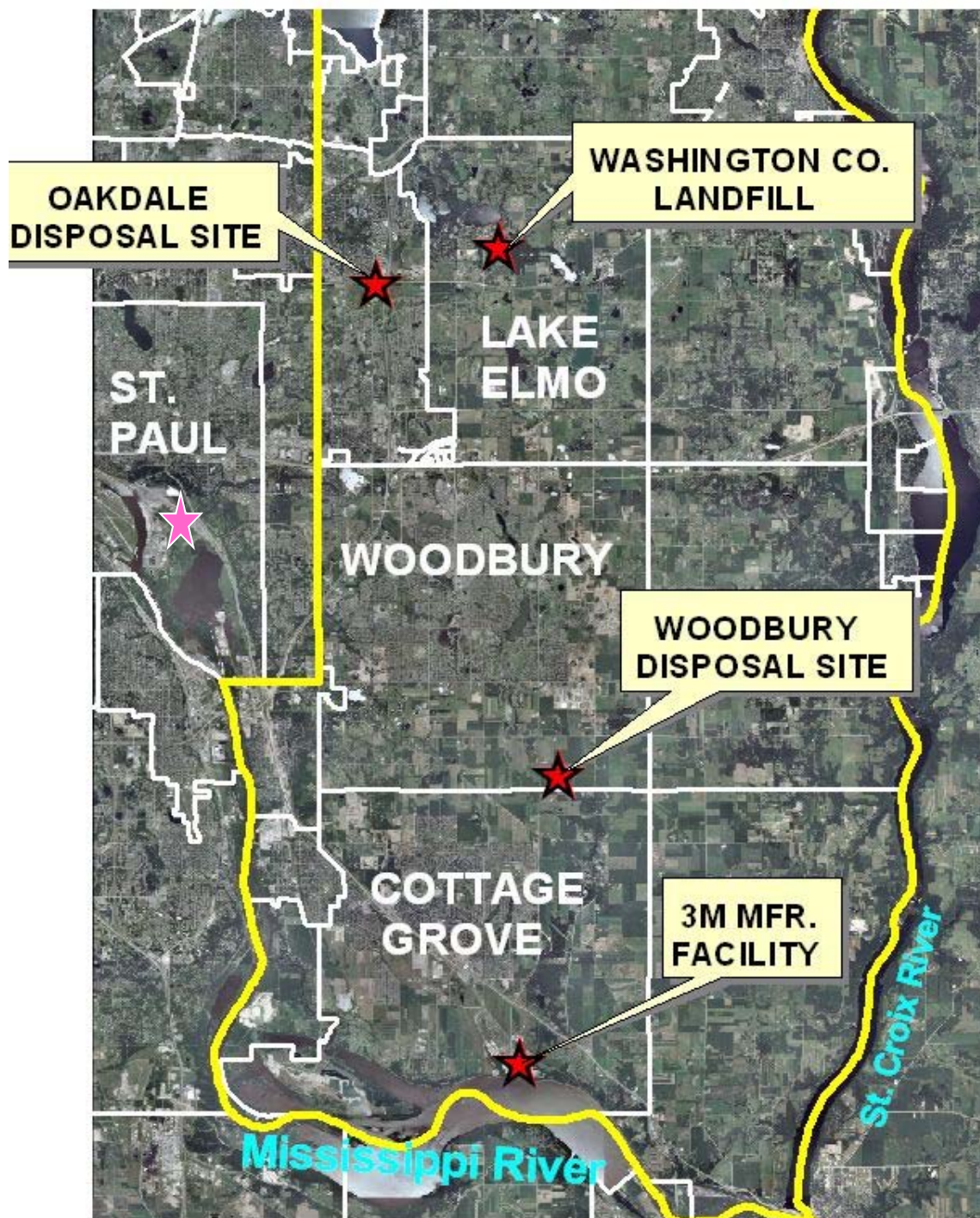


FROM: 3M

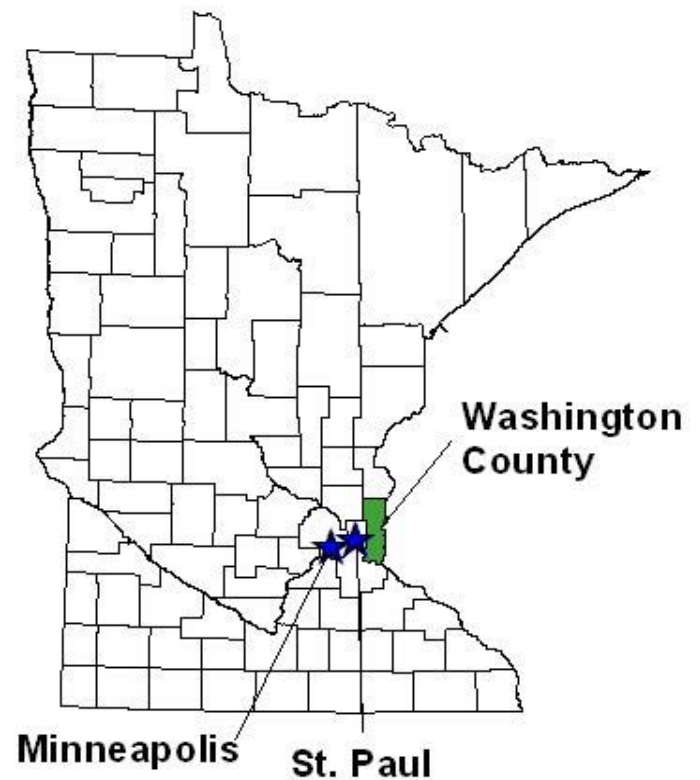
History of PFAS in Minnesota

- Washington County Landfill
 - In operation 1969-1975
 - Used by 3M
- PFAS detected private and municipal drinking water wells 2004
 - Increased monitoring
- Cessation of drinking water exposure
 - Bottled water, GAC home filters, (clean) municipal water, municipal treatment plant with GAC filters
- Drinking water guidelines
 - Health based values





LOCATION OF 3M SITES IN WASHINGTON CO. MINNESOTA

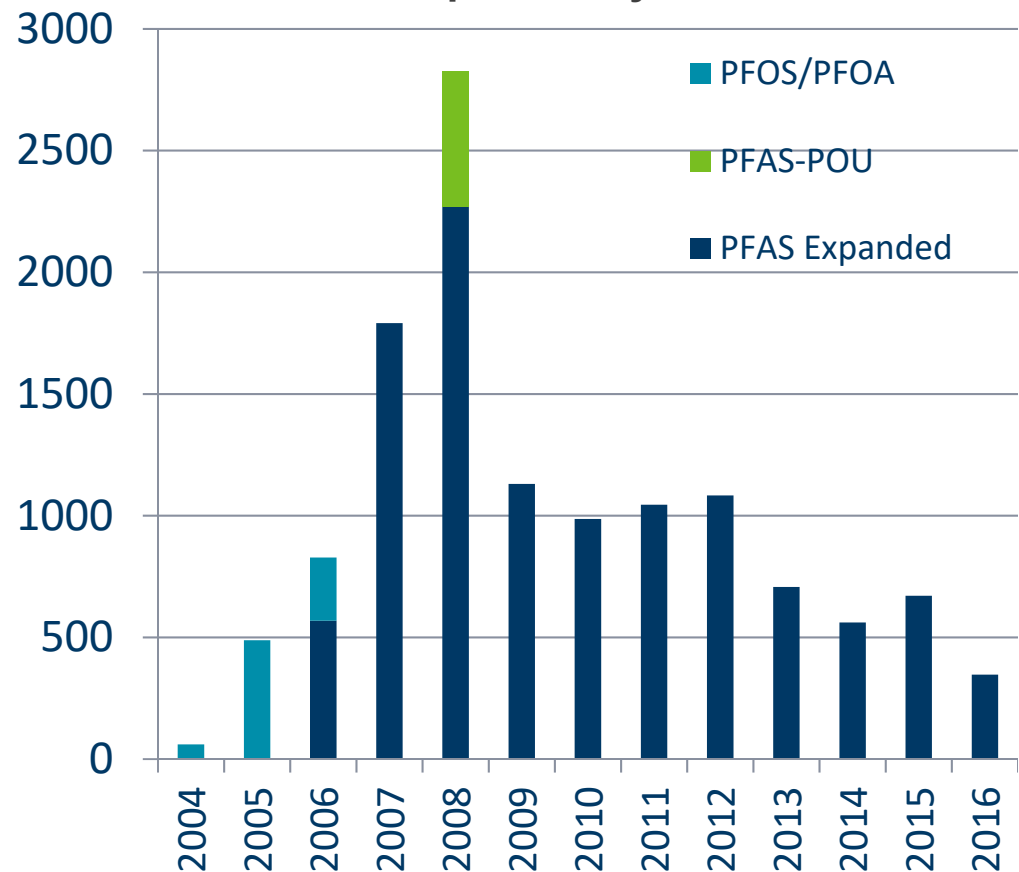


Drinking Water Analysis

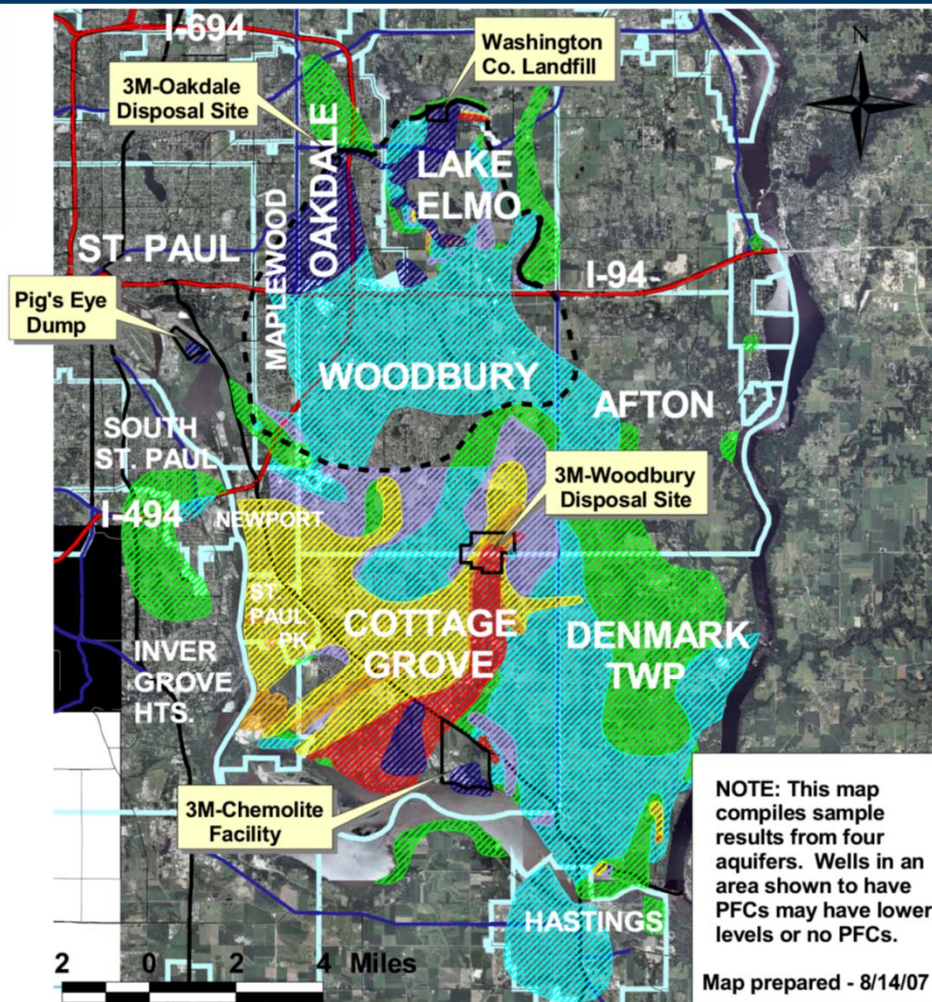
- LC/MS/MS Method

- Direct injection
- RP chromatography
- Isotope dilution quantitation
- Report levels:
 - 2007: 300ng/L
 - 2016: 25-50ng/L
- Method Performance
 - Precision
 - 2-7%
 - Accuracy
 - 99-106%

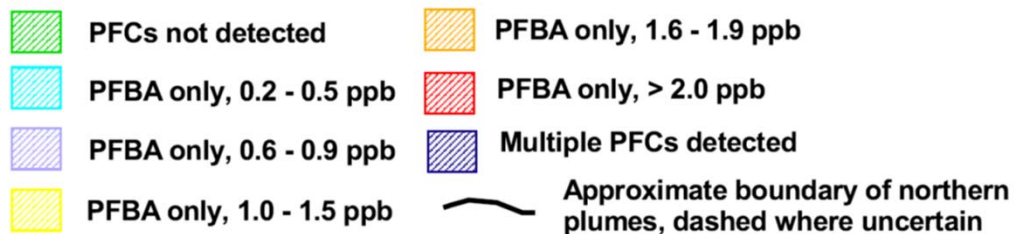
Annual samples analyzed 2004-2016



2007 Map



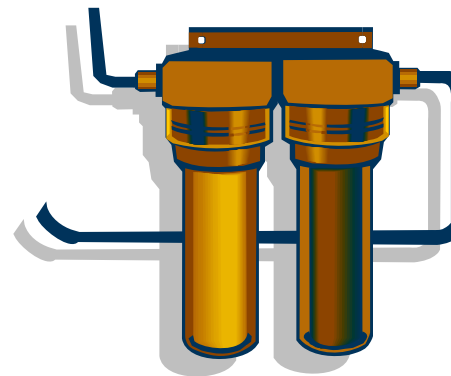
PFCs in the Southeast Metro Area



- PFOA, PFOS, PFBA detected in ground water
- PFBA most widespread

Water Clean Up Activities

- Landfills
 - On-site treatment
 - Re-line site
 - Screen other sites
- Community Systems
 - GAC
 - Breakthrough monitoring
 - PFAS interactions
- Private Wells
 - Point-of-Use Filtration report
 - GAC
 - RO



Minnesota Environmental Health Tracking and Biomonitoring Legislation (2007)

- Establish Environmental Health Tracking and Biomonitoring Program
- Conduct a pilot biomonitoring program of 4 projects
 - Include 2 communities “likely to be exposed” to PFAS
 - Required inclusion of PFBA
- Created Scientific Advisory Panel

Biomonitoring Pilot: 2008

- Participant recruitment
 - Randomly sampled from water billing records
 - Required residence prior to 2005
- 196 residents participated
 - 98 private well users, 98 municipal drinking water users
- Questionnaires used to get more data on exposure routes
- Local clinic used to collect and process specimens
 - MDH lab trained clinic for collection of serum
 - PFAS analysis at MDH



Biomonitoring Results 2008

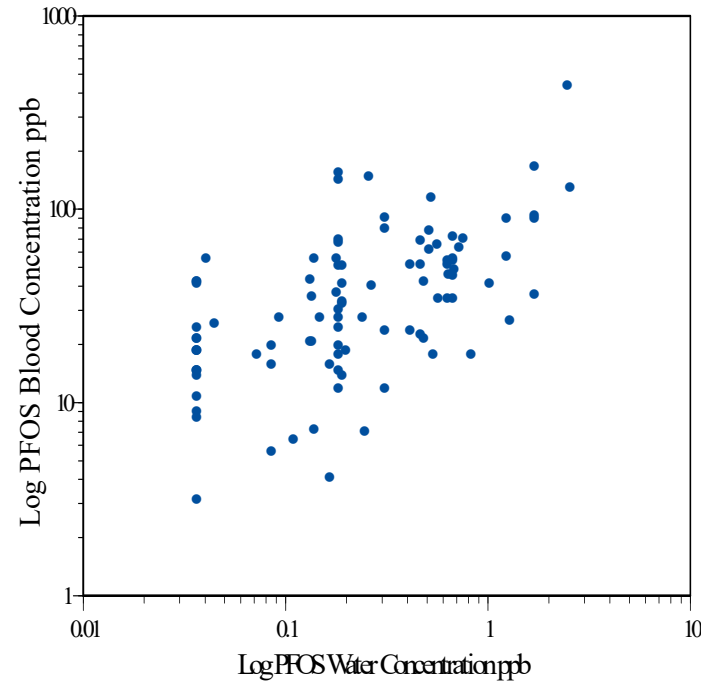
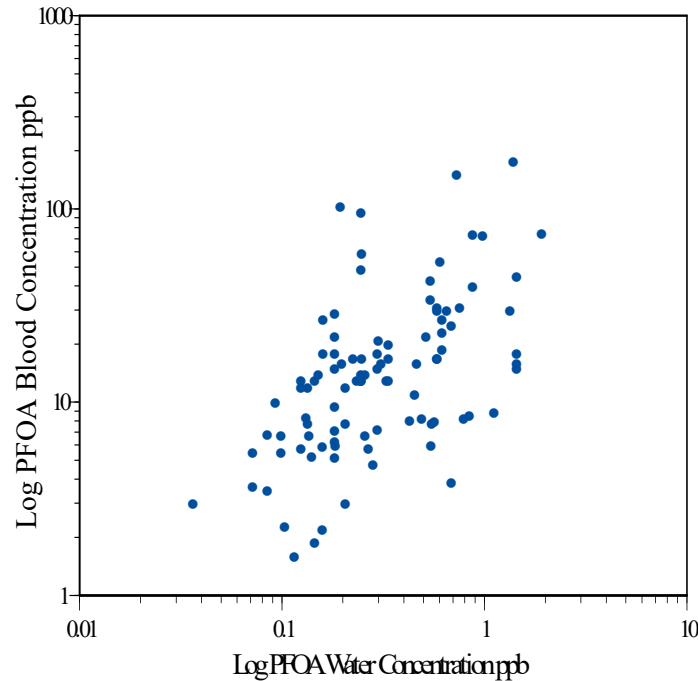
- PFOA, PFOS, PFHxS
 - Detected all 196 samples
 - Higher than NHANES
- PFOA, PFHxS, PFOS
 - Higher in men
 - Concentrations increased with age
- PFOA, PFOS associated with drinking water

	percent detection	GM (ng/ml)	NHANES (2007-2008) GM(ng/ml)
PFBS	3	NA	*
PFHxS	100	8.4	1.95
PFOS	100	35.9	13.2
PFBA	28	NA	-
PFPeA	0	ND	-
PFHxA	0	ND	-
PFOA	100	15.4	4.12

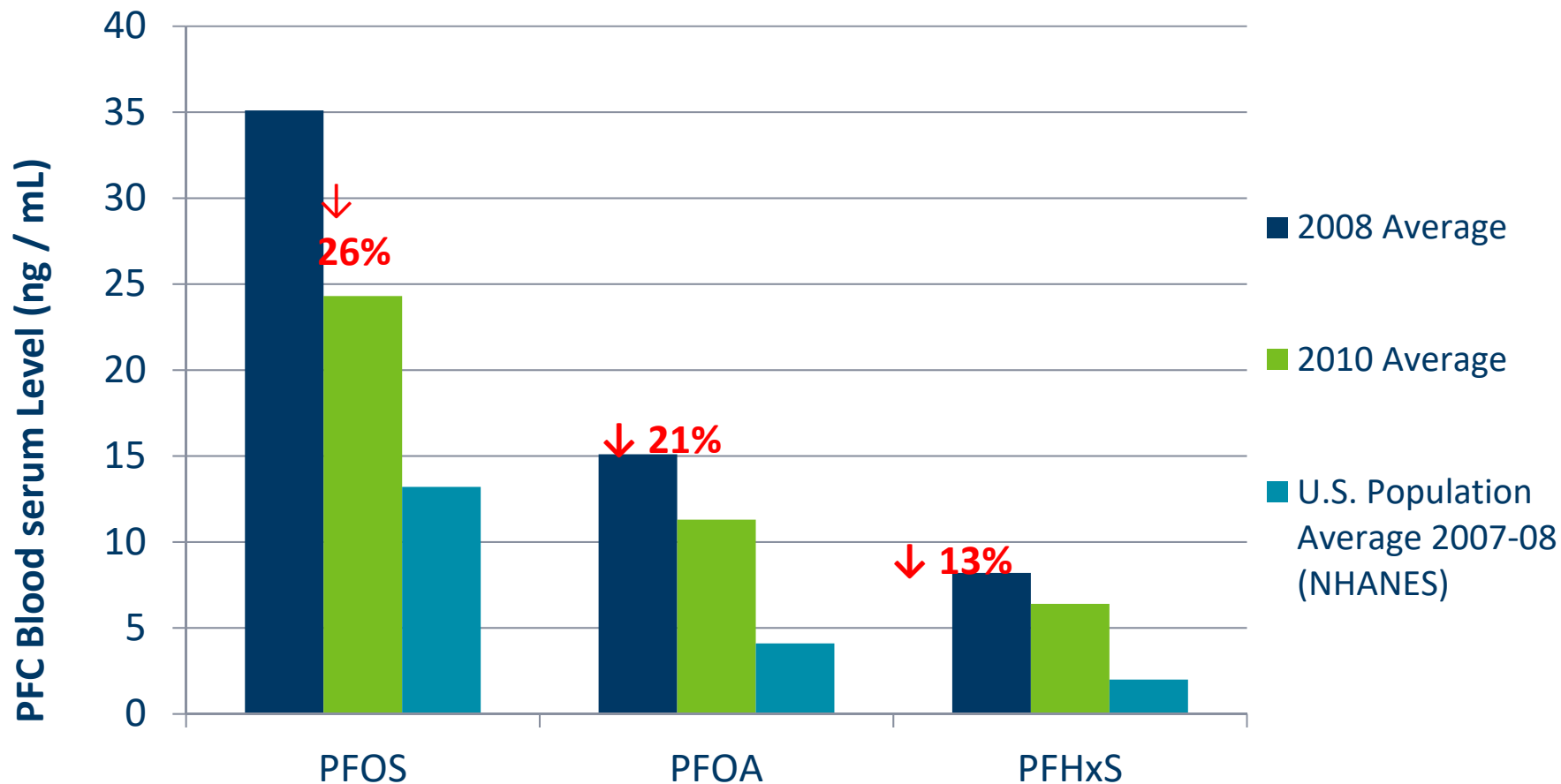
Landsteiner et al, J Env Health, 2014

2008 Blood Levels Related to Drinking Water Levels

- Analysis of a subset of private well users (n=98)



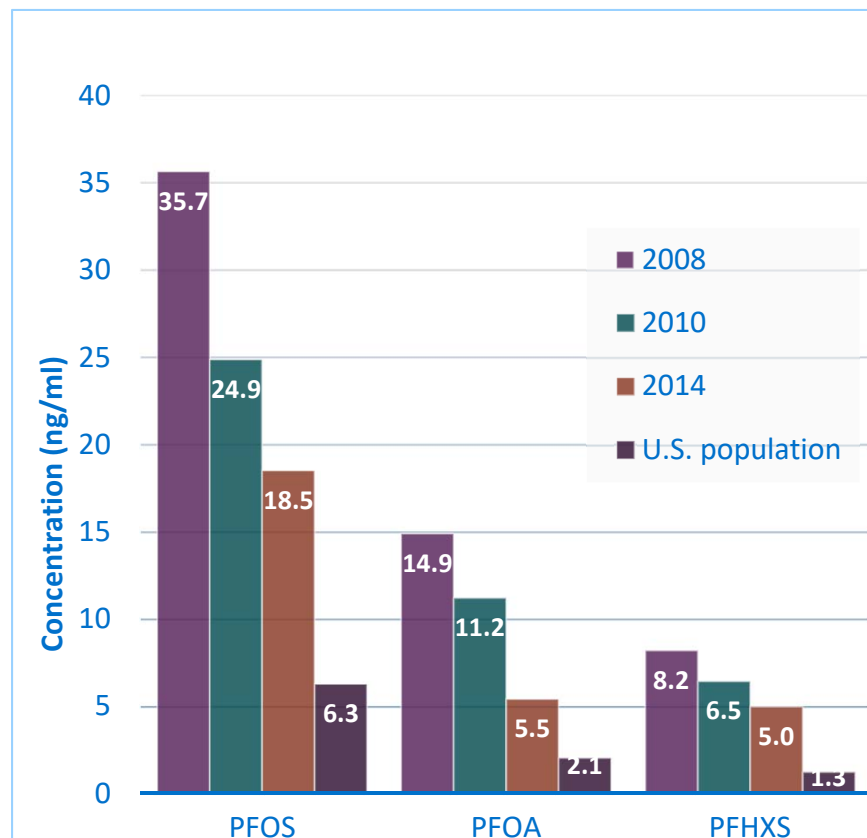
Biomonitoring Follow Up: 2010



Note on PFBA Detects: 2008 = 25%; 2010 - 21%

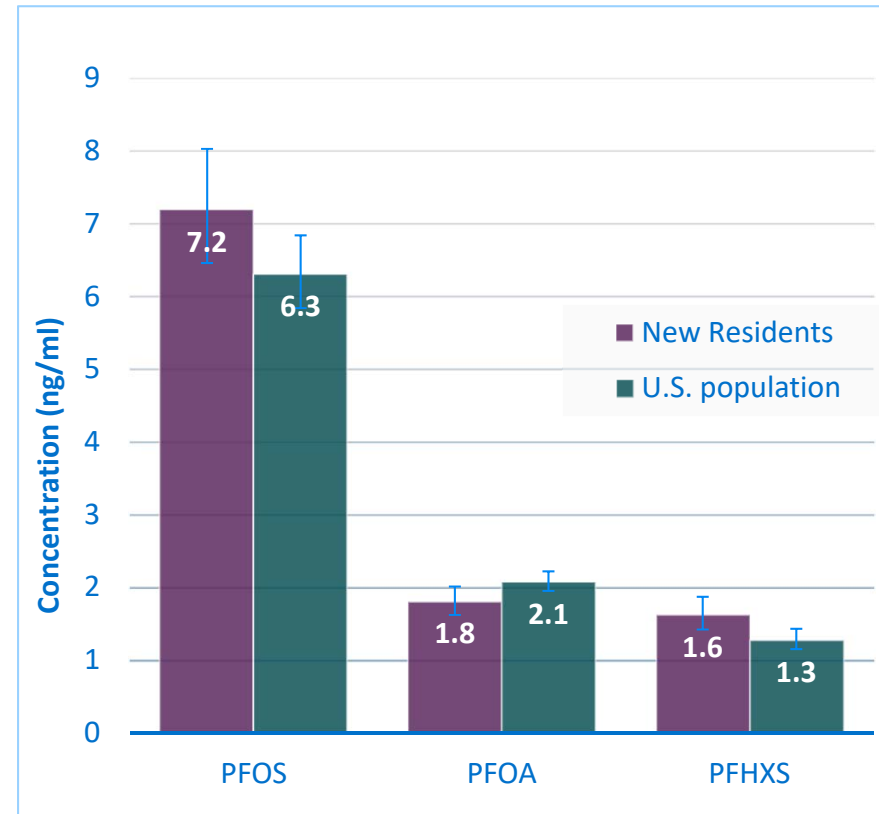
2008, 2010, 2014 Blood PFAS levels compared to NHANES

- Blood levels of long term residents on the decline
- Mean individual percent change 2008-2014 (n=149)
 - PFOS 45% decrease
 - PFOA 59% decrease
 - PFHxS 34% decrease
- Intervention was effective to reduce exposure



PFAS in New Residents (2014)

- New residents (n=156)
 - Moved to community after intervention
- Compared to NHANES 2011-2012
 - No significant difference in levels between groups



Serum Analysis

- Method used in 2008 & 2010- Based on Kuklenyik, 2004

- Uses 1ml serum
- SPE cartridges

- Method used in 2014 - similar to Flaherty, 2005

- 400uL serum
- Protein precipitation
- 96 well plate

- Both methods:

- Matrix matched calibration curves & ID
- Reversed phase HPLC/MS/MS
- Report level: 0.1 ng/mL

- Method Performance

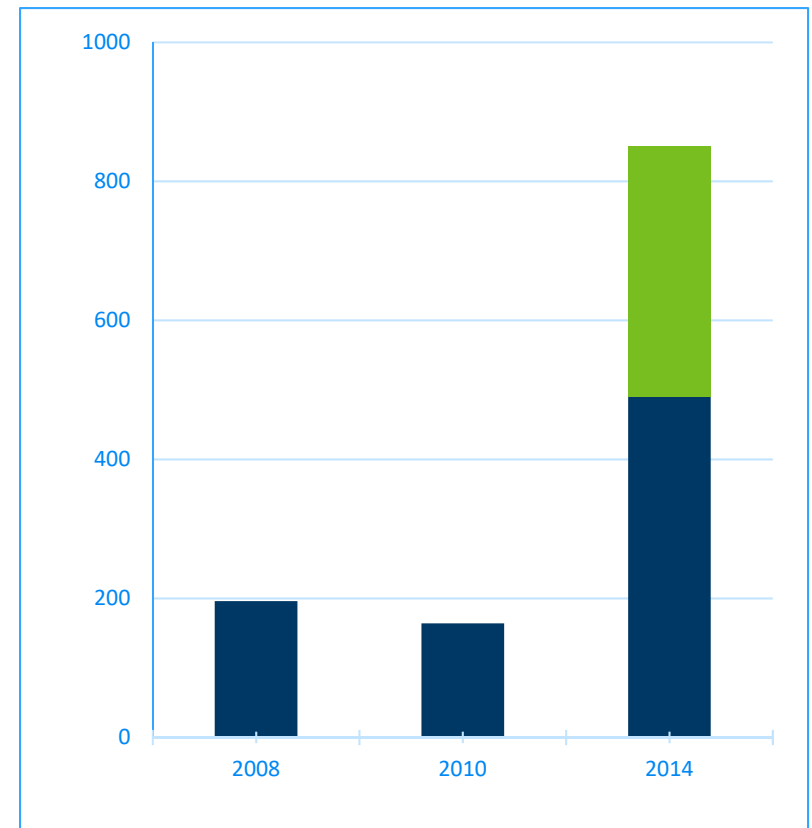
- Archived 2008 samples used to validate 2014 method

- $\pm 20\%$ RPD

- Precision and Accuracy

- 2008/2010: 2-8%, 100-115%
- 2014: 1-8%, 99-115%

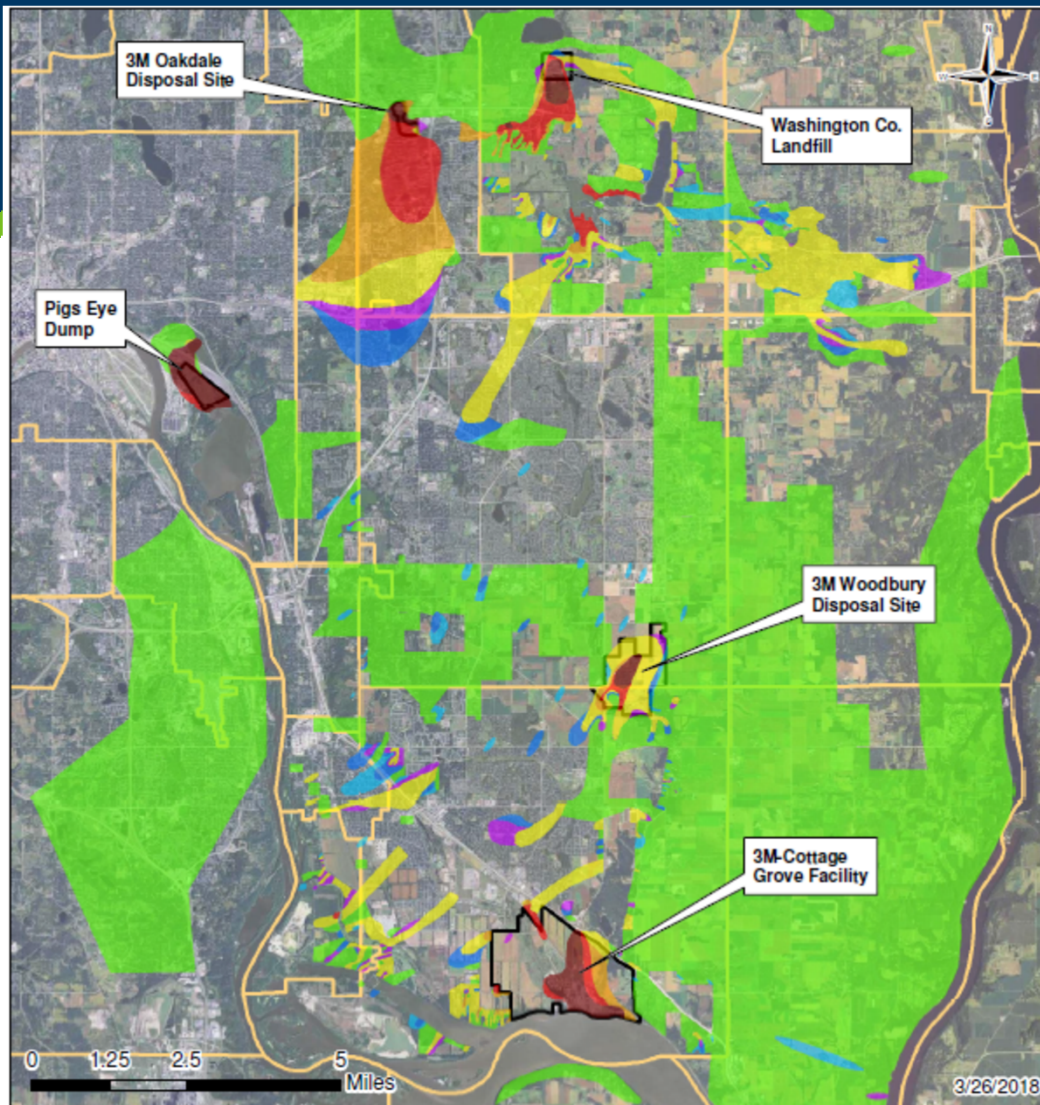
Number of samples analyzed



Biomonitoring Summary

- Biomonitoring projects answered questions from community and legislature
 - PFAS blood levels declining in population with prior exposure
 - PFAS blood levels in new residents comparable to US population
 - Mixed success in teasing out sources of exposure

Current Maps



PFOA - All Aquifers March 2018

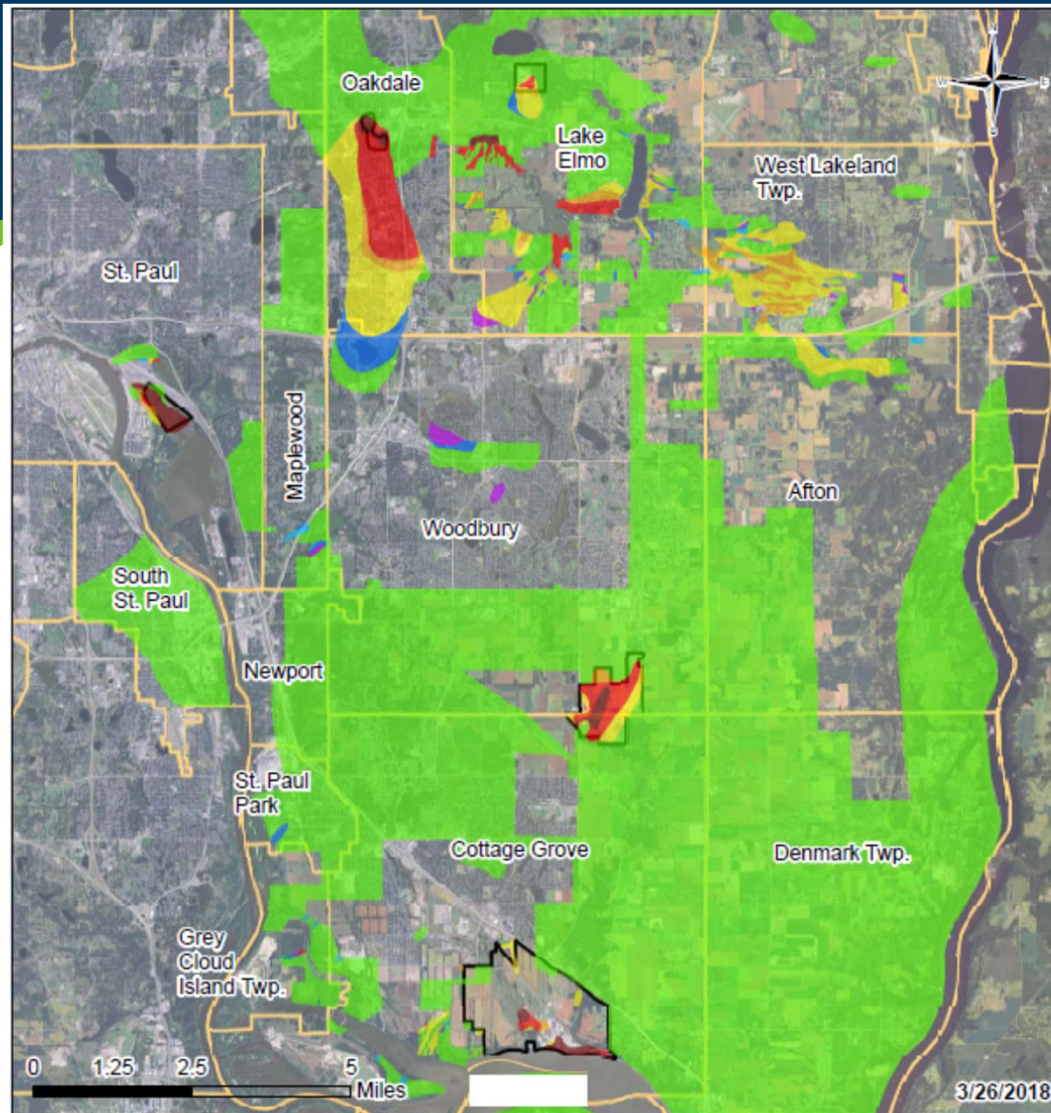
Phone: 651-201-4897
or 1-800-657-3908

PFOA greater than 1.75ppb (>50x HBV)	PFOA 0.027-0.035ppb (75-100% HBV)	MDH Health Based Value (HBV) for PFOA is 0.035 parts per billion (ppb; or 35 parts per trillion)
PFOA 0.35-1.75ppb (10-50x HBV)	PFOA 0.0175-0.026ppb (50-75% HBV)	
PFOA 0.175-0.35 ppb (5-10x HBV)	PFOA 0.004-0.0174ppb (<50% HBV)	
PFOA 0.035-0.175ppb (1-5x HBV)	PFOA not detected	

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

- PFOA - March 2018
- 5 main sources
 - Oakdale Disposal Site
 - Washington County Landfill
 - Pigs Eye Dump
 - 3M Woodbury Disposal Site
 - 3M Cottage Grove Facility
- PFOA HBV 0.035 ng/ml

Current Maps



PFOS - All Aquifers - March 2018 Phone: 651-201-4897 or 1-800-657-3908

DEPARTMENT OF HEALTH

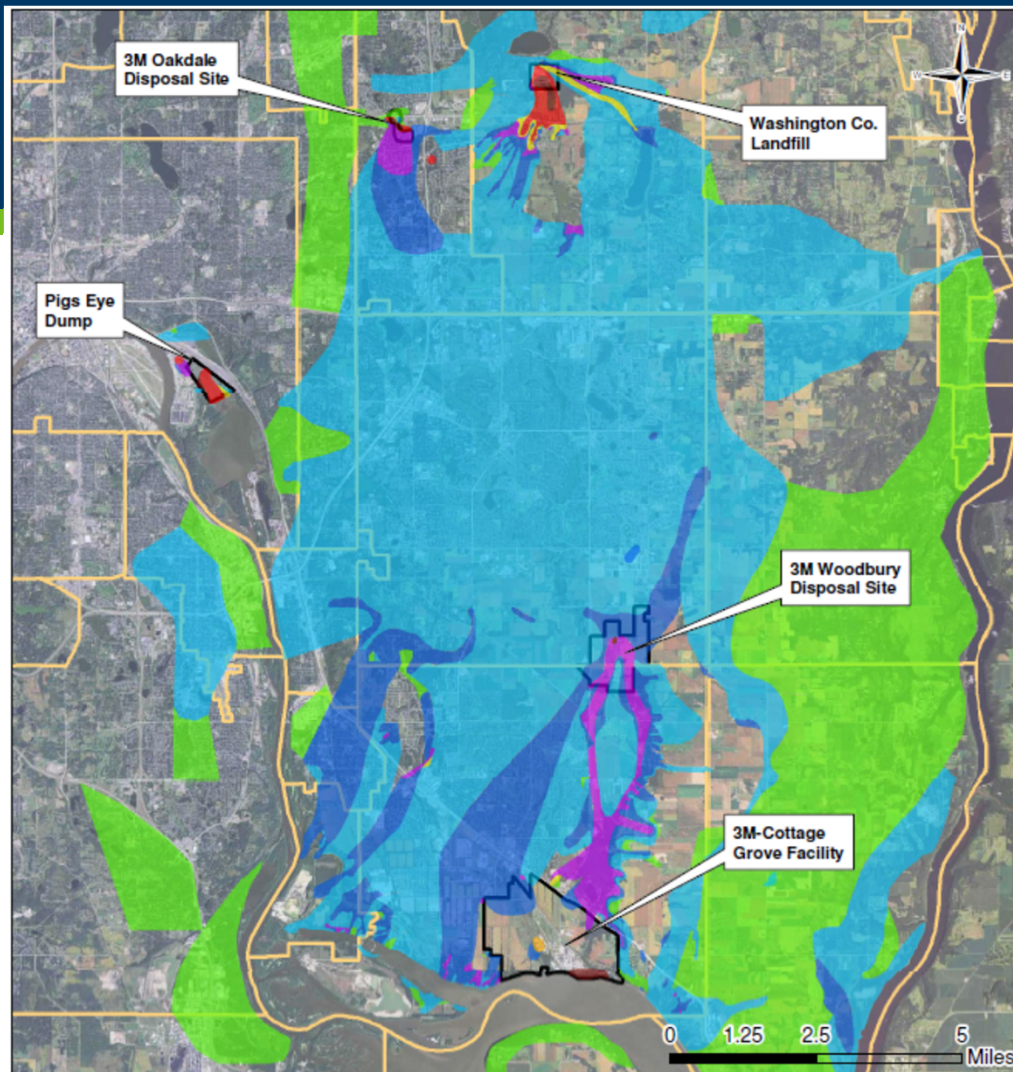
PFOS greater than 1.35ppb (>50x HBV)	PFOS 0.021-0.027ppb (75-100% HBV)
PFOS 0.271-1.35ppb (10-50x HBV)	PFOS 0.0136-0.02ppb (50-75% HBV)
PFOS 0.136-0.27ppb (5-10x HBV)	PFOS 0.004-0.0135ppb (<50% HBV)
PFOS 0.028-0.135ppb (1-5x HBV)	PFOS not detected

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

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

- PFOS as of March 2018
- 5 main sources
 - Oakdale Disposal Site
 - Washington County Landfill
 - Pigs Eye Dump
 - 3M Woodbury Disposal Site
 - 3M Cottage Grove Facility
- PFOS HBV 0.027 ng/ml

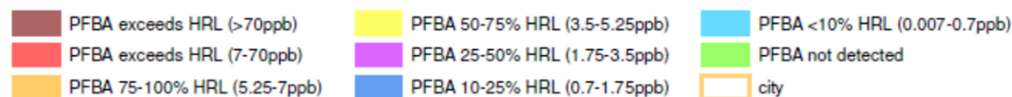
Current Maps



PFBA - All Aquifers

March 2018

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



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

- PFBA - March 2018
- 5 main sources
 - Oakdale Disposal Site
 - Washington County Landfill
 - Pigs Eye Dump
 - 3M Woodbury Disposal Site
 - 3M Cottage Grove Facility
- PFBA HRL 7 ng/ml

Acknowledgements

- MDH Environmental Public Health Tracking and Biomonitoring Program Staff
 - Adrienne Landsteiner, MPH, PhD Epidemiologist/Project Coordinator
 - Christina Rosebush, MPH Epidemiologist/Project Coordinator
 - Jessie Shmool, PhD Epidemiologist/Program Director
- MDH Environmental Health
 - Ginny Yingling, MS Hydrogeologist
 - Helen Goeden, PhD Toxicologist
 - Julie Kadrie, MPH Health Risk Communications
 - Mike Convery, PG Hydrogeologist
- MDH PHL
 - Marty Bevan, PhD Research Scientist
 - Kitrina Barry, MS Research Scientist
- Thank you to APHL for the travel funding

For More Information

- PFAS in Minnesota
 - <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html>
- Minnesota Environmental Health Tracking and Biomonitoring Program
 - <http://www.health.state.mn.us/divs/hpcd/tracking/biomonitoring/index.html>

References:

Buck et al, Integrated Environmental Assessment and Management, 2011, 7(4), 513-541

Flaherty et al, Journal of Chromatography B, 2005, 819, 329-338

Kuklenyik et al, Environmental Science and Technology, 2004, 28, 3698-3704

Landsteiner et al, Journal of Environmental Health, 2014, 77(5), 14-19

Questions?