PFAS in West Michigan: What We Know and Should We Be Concerned?

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Annis Water Resources Institute

How did I get involved……

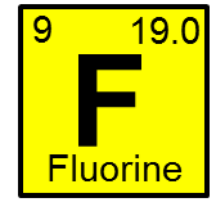
- 2011. Citizen's group (CCRR) complains to EPA that the Wolverine World Wide Tannery was demolished without out proper oversight.
- 2012. EPA initiates site review, conducts sampling, and the site does not score high enough to be listed in Superfund. MDEQ and WWW agree to conduct further investigations
- 2013. Asked by a citizen's group to review data concerning the Rockford Tannery demolition and wrote a memo raising concerns. MDEQ and Rockford say they will not listen to CCR because of extremist views and has WMAC serve as intermediary. WWW states no disposal or chemical records remain for the Tannery.
- 2014. I became concerned about PFAS at the site due to the use of historic use of Scotchgard. Checked with MDEQ and asked about PFAS testing of fish in the Rogue River

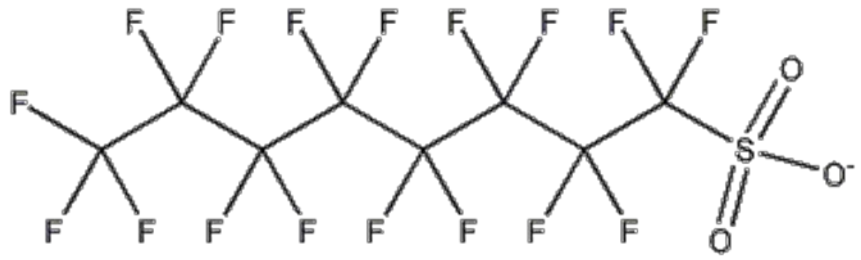
How did I get involved……

- 2014. MDEQ confirms that PFAS was present in the fish and will be developing consumption guidelines. CCRR finds city of GR has chemical usage records and finds Scotchgard listed on MSDS and Spill Plan records
- 2015. MDEQ issues fish consumption advisory for PFAS in the Rogue but were too busy with Wurthsmith AFB to do more studies. Expressed concerns to WMEAC about PFAS.
- 2016. WMEAC sets up meeting with WWW about PFAS and other issues. WWW and their consultant deny PFAS was used at the site. CCRR identifies House Street as a former disposal site and does interviews of residents and former employees.
- 2017. I wrote a memo to MDEQ with multiple pieces of evidence that PFAS may be present and called for immediate investigation of the Tannery and offsite disposal sites. WWW agrees to do testing in the Fall.
- 2018. Meeting with State Representatives and EPA.

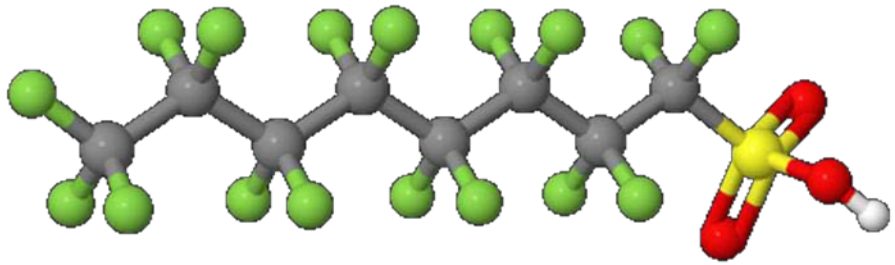
Introduction to PFAS

- **PFAS - Per- and Polyfluoroalkyl Substances**
- Synthetic organic compounds that contain multiple Fluorine (F) atoms.
- 2 most studied PFAS are
  - Perfluorooctanoic Acid (PFOA)
  - Perfluorooctane Sulfonate (PFOS)
- PFAS family = thousands of diverse compounds





Conder et al. (2008)

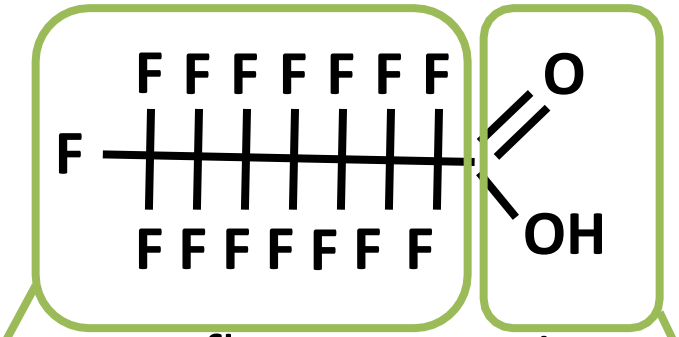


Chemspider

Example molecular structures for perfluorooctane sulfonate (PFOS)

From: Hillary Thornton, USEPA Region 4

PFAS – A class of chemicals



perfluorooctanoic acid (PFOA)

Fluorocarbon tail

- Strong bonds
- Repels oil and water
- Varying length

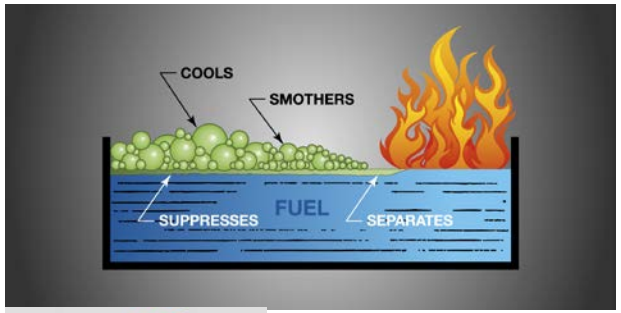
Functional group

- Strong to weak acids
- Dissolves in water

Products

SCOTCHGARD™ PROTECTOR 3M

For Leather



Scotchgard contained

- PFOS Perfluorooctanesulfonic acid
- PFOA Perfluorooctanoic acid

Teflon was a PFOA based polymer

Teflon® Industrial Coatings DUPONT

STAINMASTER® BRAND Live well™

SIMONIZ®

GUARANTEED TO KEEP YOU DRY
GORE-TEX® PRODUCTS
GORE

Expansive Use of PFAS

Commercial Products	**Industrial Uses**
Cookware (Teflon®, Nonstick) Fast Food Containers Candy Wrappers Microwave Popcorn Bags Personal Care Products (Shampoo, Dental Floss) Cosmetics (Nail Polish, Eye Makeup) Paints and Varnishes Stain Resistant Carpet Stain Resistant Chemicals (Scotchgard®) Water Resistant Apparel (Gore-Tex®) Cleaning Products Electronics Ski Wax Soil amendments Pesticides Potting soils	Photo Imaging Metal Plating Semiconductor Coatings Aviation Hydraulic Fluids Medical Devices Class B Firefighting Foam (e.g., Aqueous Film Forming Foam) Insect Baits Printer and Copy Machine Parts Chemically Driven Oil Production Textiles, Upholstery, Apparel and Carpets Paper and Packaging Rubber and Plastics Pesticides

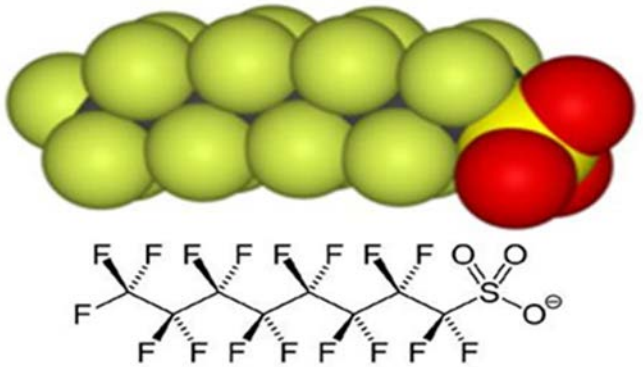
PFAS –Timeline

Date	Event
1956	3M begins selling Scotchgard Protector containing PFOS and PFOA
1958	Wolverine begins to produce Hush Puppies shoes in Rockford Michigan using Scotchgard
1978	3M finds PFAS in employees blood and finds it is toxic to monkeys
1998-9	Studies find PFOS is present in human blood and wildlife. Reports of toxicity and bioaccumulation published in scientific literature
2000	3M announces the phase out of Scotchgard due to environmental and human health concerns. Reports sent to customers, many media stories
2001	Research shows perfluorinated chemicals are present in birds and wildlife around the planet
2002	3M stops producing Scotchgard. DuPont continues production, China increases production. More media articles are published about the hazards of PFOS. EPA says new data suggest potential for reproductive/developmental toxicity, and that blood samples suggest unexplained exposure to general public.

PFAS –Timeline

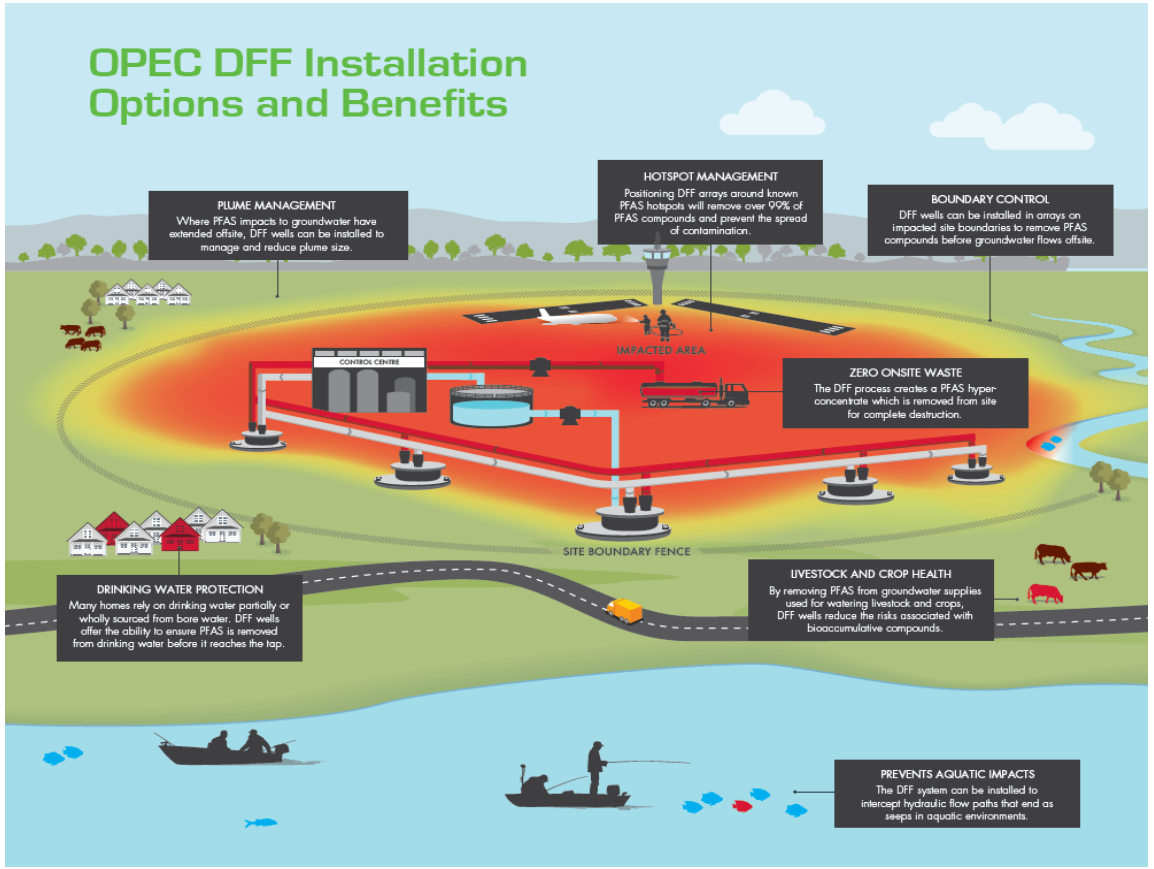
Date	Event
2006	DuPont announces phase out of C8 by 2015. Major class action suit and scientific research
2007	PFOS/PFOA found in 98% of US blood samples (Calafat et al) Levels decreased after 3M discontinued production
2008-9	EPA publishes Method 537 for PFOS/PFOA and related chemicals
2009	EPA Provisional Health Advisory Short-term adverse health effects PFOS: 200 ppt, PFOA: 400 ppt
2012	EPA requires drinking water to be monitored
2013	PFAS detected in Plainfield Well Water 50-60 ppt
2015	MDEQ reports PFAS in fish from the Rogue River near the Tannery
May 2016	EPA Health Advisory Long-term adverse health effects PFOS + PFOA: 70 ppt
2016	PFOS detected in Plainfield Well Water at 7.9 ppt and PFOA at 2.6 ppt.
2017	Widespread groundwater problems in the Rockford area discovered due the disposal of Wolverine World Wide industrial wastes on farm land and gravel pits

PFAS Challenges



Unique chemical properties

- Highly mobile and persistent in the environment.
- Bioaccumulates in fish and plants log Kow ~ 4.81
- Challenging to remediate – not biodegradable. Only activated carbon will effectively remove PFAS from water.



https://opecsystems.com/files/OPEC_Systems_PFAS_Solutions.pdf

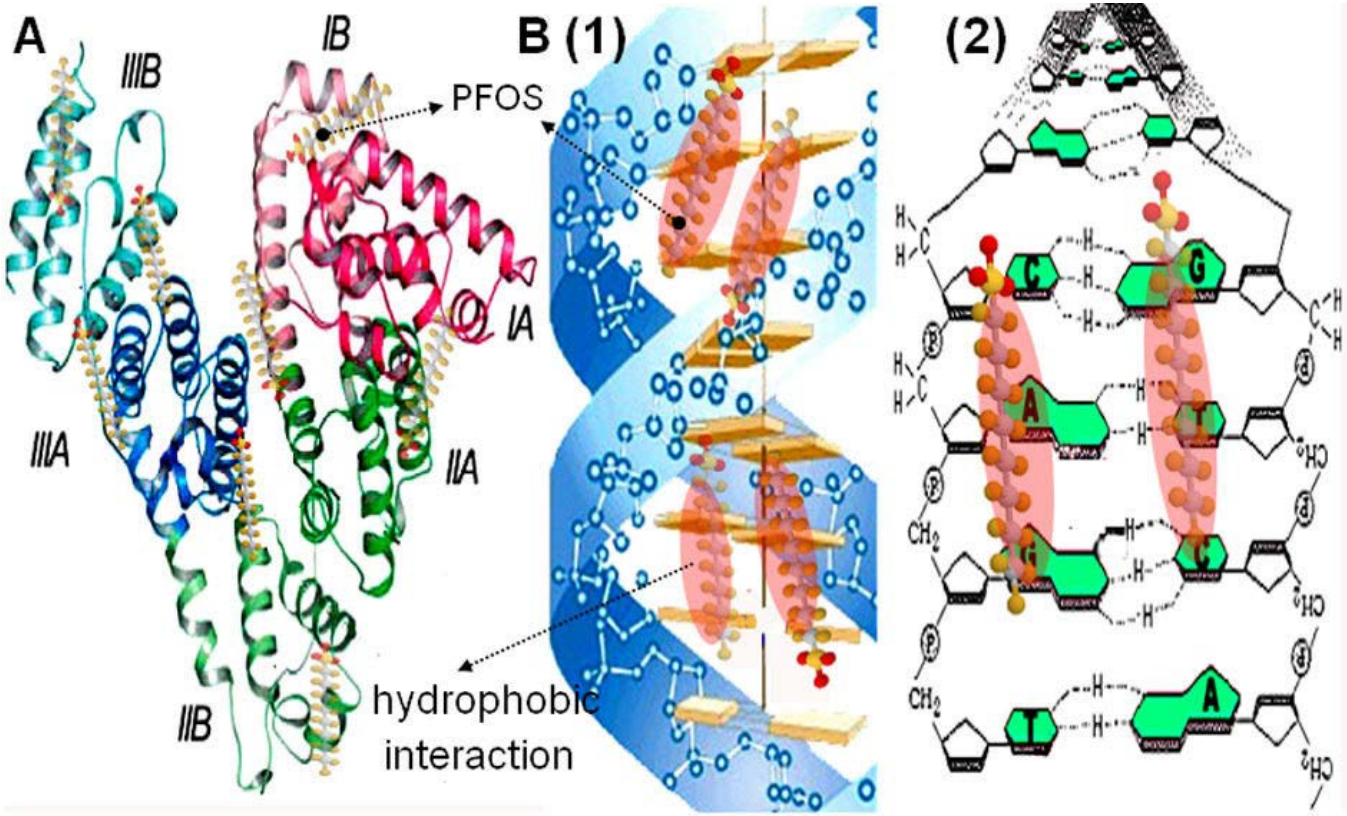
PFAS Challenges

Health impacts

- Known or suspected toxicity at very low concentrations
- Binds to proteins and DNA
- Long half-lives (several years) in humans
- Sensitive receptor endpoint (resemble Fatty Acids)

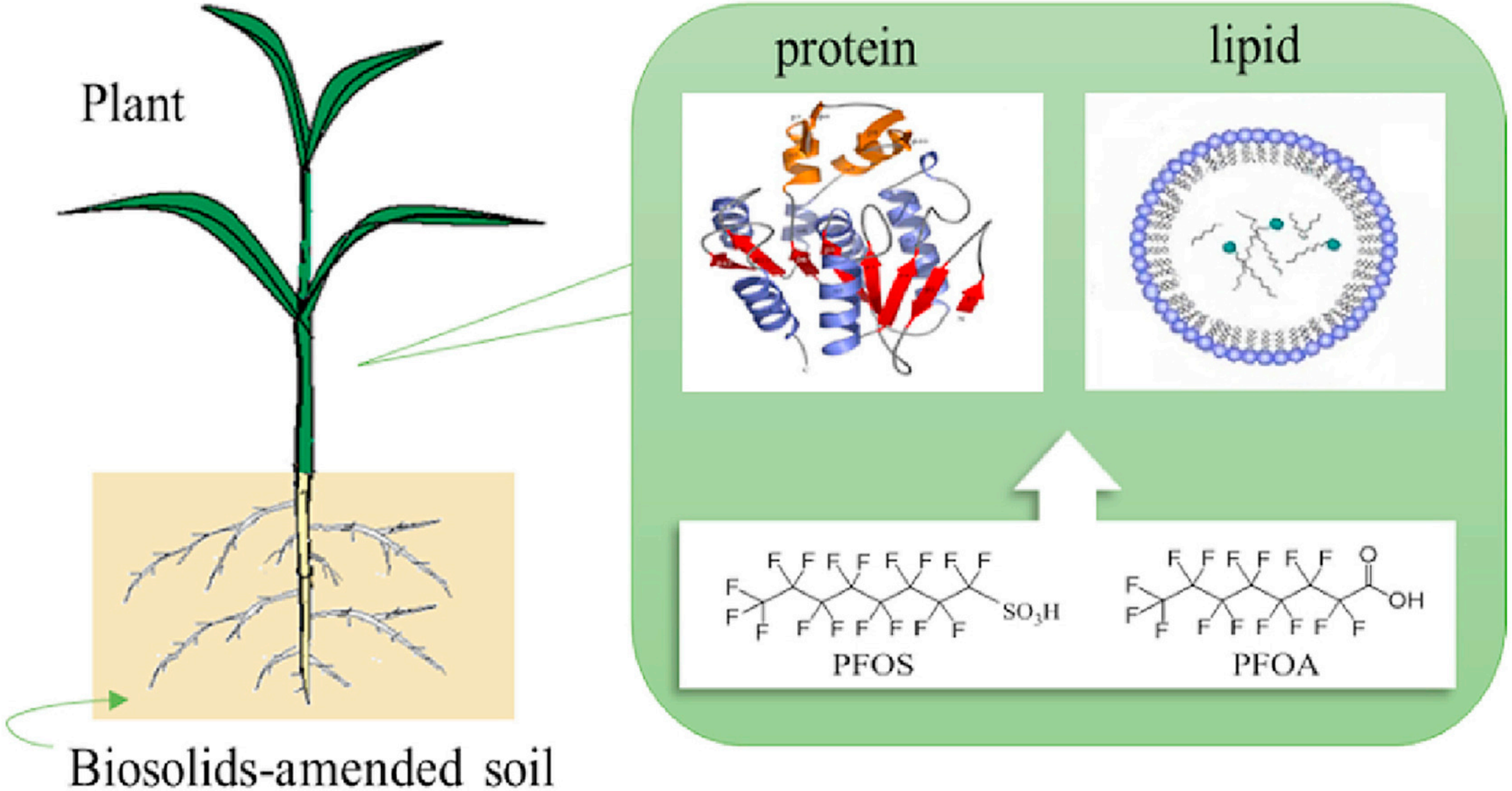
Analytical technology rapidly evolving

Wide geographical impact with heightened public awareness



Zhang 2009

Translocation from Soil to Plants

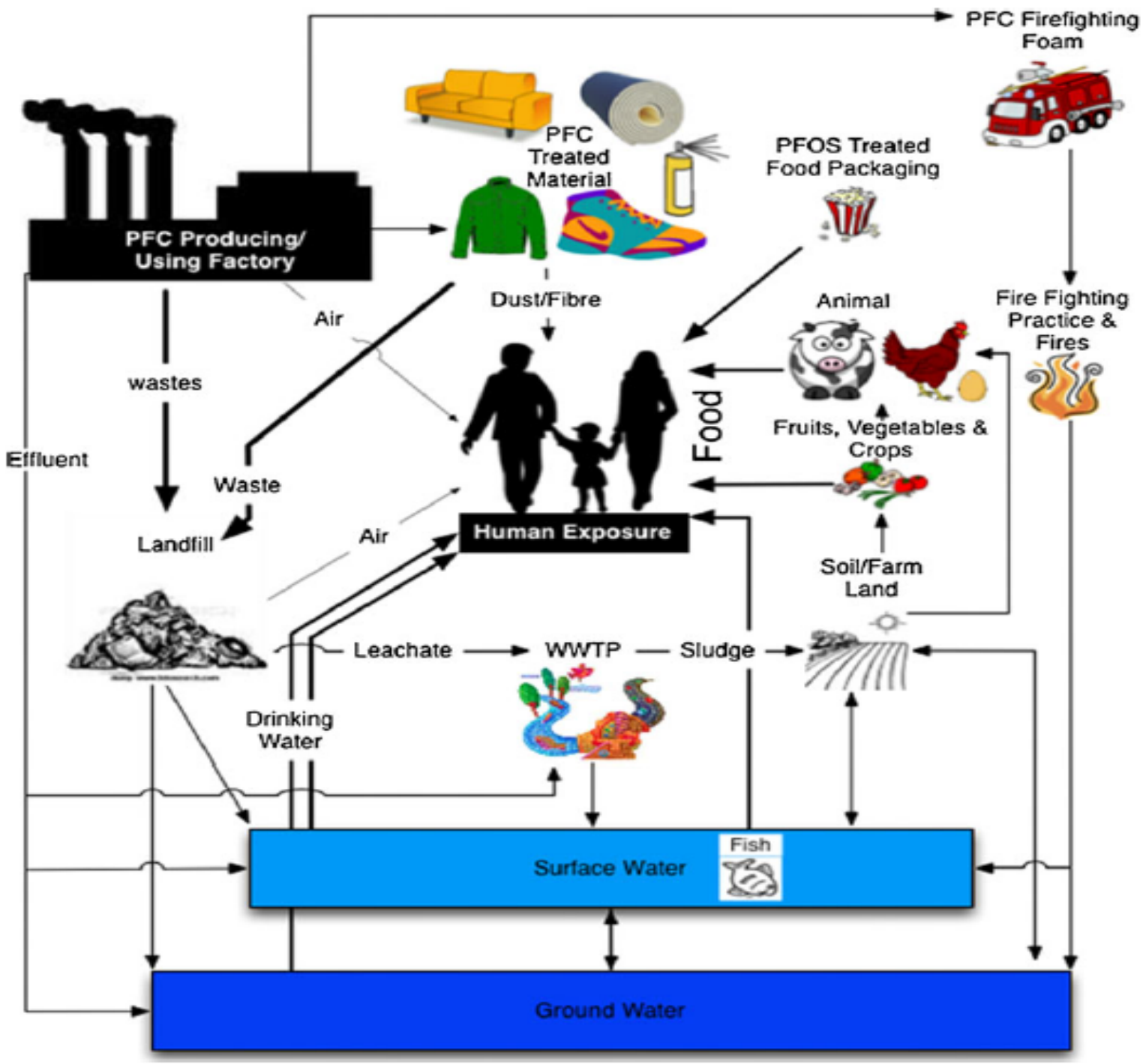


Wen et al, 2016

Examples of Chemical Challenges

- Groundwater in Cities – public water
- Polychlorinated dibenzo(p)dioxins and furans
- Mercury
- Arsenic and lead in drinking water
- Formaldehyde in air
- Radon
- Commonality: Background exposure levels are of similar magnitude to “risky” levels

PFAS in the Environment

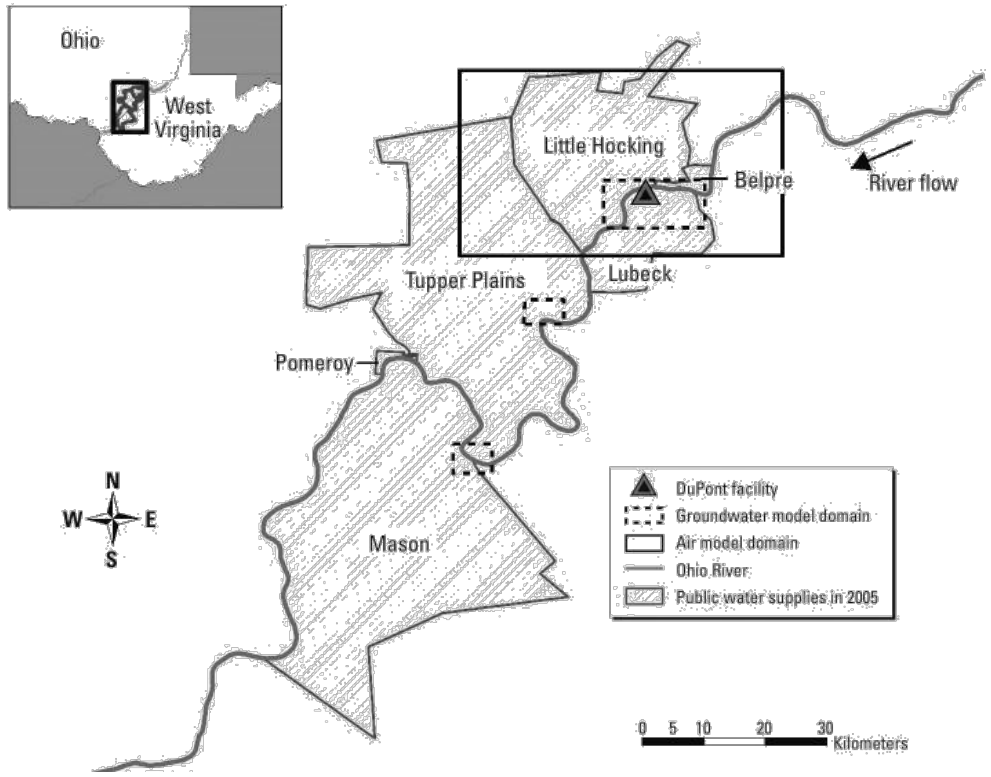


Oliaei 2013

C8 Science Panel Studies Dupont

http://www.c8sciencepanel.org/prob_link.html and Shin et al (2011). Environ Health Perspect. 119(12):1760–1765.

- Focused on PFOA from Dupont's Washington Works facility in Wood County, WV
- Conducted as a condition of a lawsuit settlement
- Populations studied
  - 69,000 Community residents of six Mid-Ohio River Valley districts with PFOA-contaminated drinking water supplies
  - Former workers at the Dupont plant
  - Combined residents and workers (for follow-up cancer studies)



C8 Science Panel Studies

http://www.c8sciencepanel.org/prob_link.html

- Probable links between PFOA exposure and:
  - Diagnosed high cholesterol
  - Ulcerative colitis (autoimmune disease)
  - Thyroid disease
  - Testicular and kidney cancers
  - Pregnancy-induced hypertension

Agency for Toxic Substances and Disease Registry ATSDR

- Affects the developing fetus and child, including possible changes in growth, learning, and behavior, low birth weight, accelerated puberty, skeletal variations.
- Hormone interference (thyroid and fertility)
- Increase cholesterol,
- Affect the immune system
- Increase cancer risk (Liver, kidney, testicular).

Endpoints Evaluated by Other Authoritative Groups

Birth Weight

- Systematic review using Navigation Guide methodology.
- Most studies are from general population (low exposure).
- **"Sufficient" human evidence for reduced fetal growth from prenatal exposure.**

Cancer

- USEPA SAB (2006) - **"likely carcinogen".**
- IARC (2015) - **"possibly carcinogenic".**
- USEPA Office of Water (2016) - **"suggestive carcinogen".**
- Associations with **kidney and testicular cancer** in communities with drinking water exposure are noted.

Immunotoxicity

- Systematic review by National Toxicology Program.
- Most studies are from general population (low exposure).
- "Moderate" level of human evidence and "high" level of animal evidence for suppression of antibody response.
- **Overall conclusion: "presumed immune hazard to humans".**

Health Assessment Challenges and Concerns

Long half life in Humans compared to test animals

- Humans 4-9 years, Rats 17-50 days

Human kidney reabsorbs PFAS

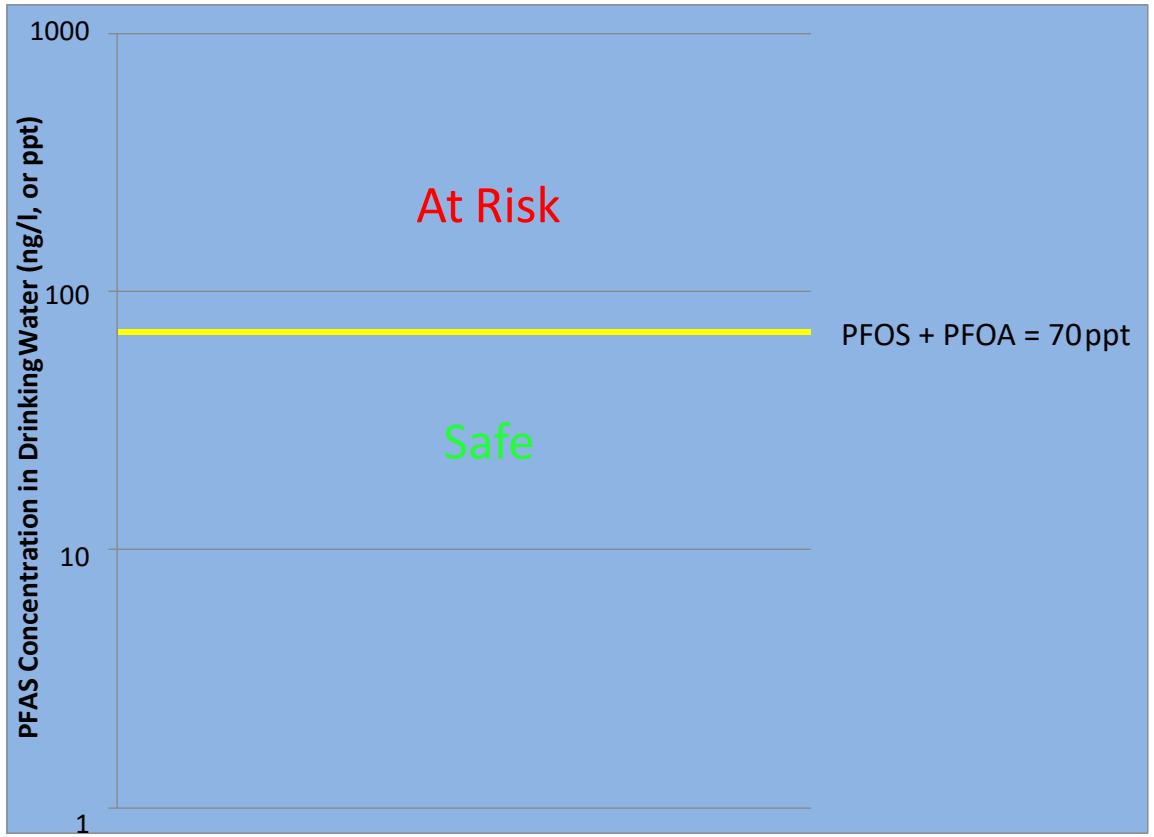
Binds to portions and stays in circulation. Humans get a higher serum dose than test animals

High maternal transfer to fetus

Source: Lau et al. 2015

What Level of PFAS in Drinking Water is Safe?

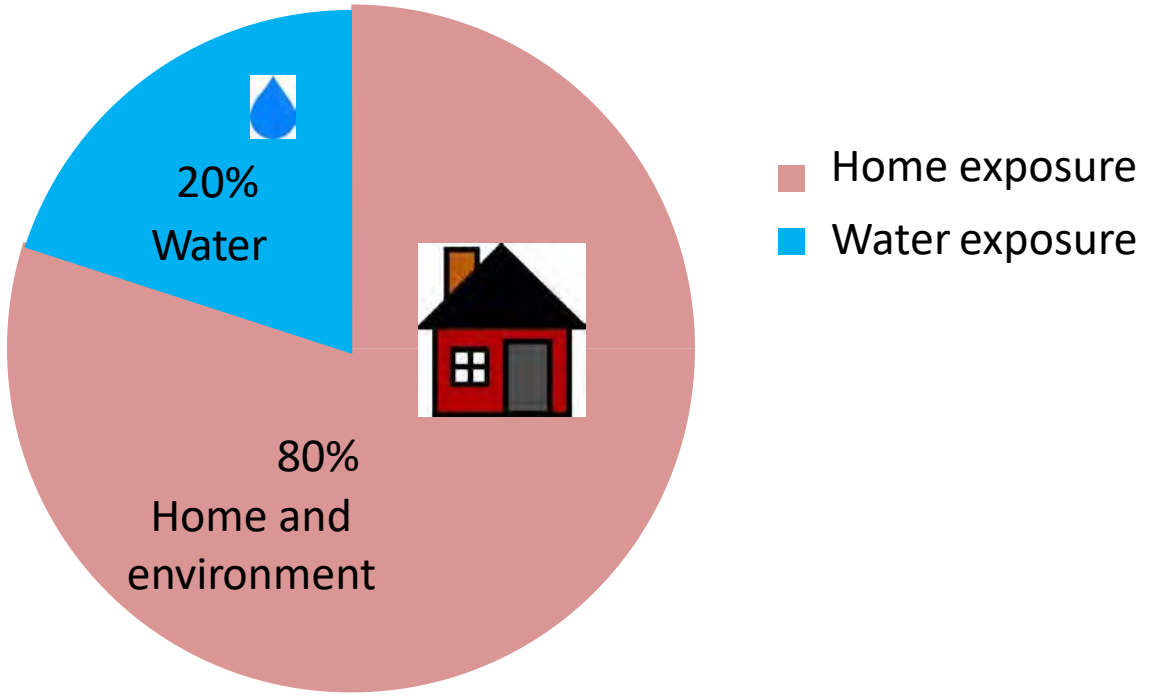
- U.S. EPA
  - January 2009
    - PFOA = 400 ppt
    - PFOS = 200 ppt
  - Early 2016
    - PFOA = 100 ppt
  - May 2016
    - PFOA + PFOS = 70 ppt
- New Jersey
  - 2009
    - PFOA = 40 ppt
  - 2016
    - PFOA = 14 ppt
- Vermont
  - March 2016
    - PFOA = 20 ppt



EPA's PFOA/PFOS health advisory: 70 ppt = 70 ng/L

Protective Factors

- **80% home/environment exposure**
  - **20% water exposure**
- **Over 70 year lifetime**
  - **2 liters per day consumption**
- **Children and lactating women**



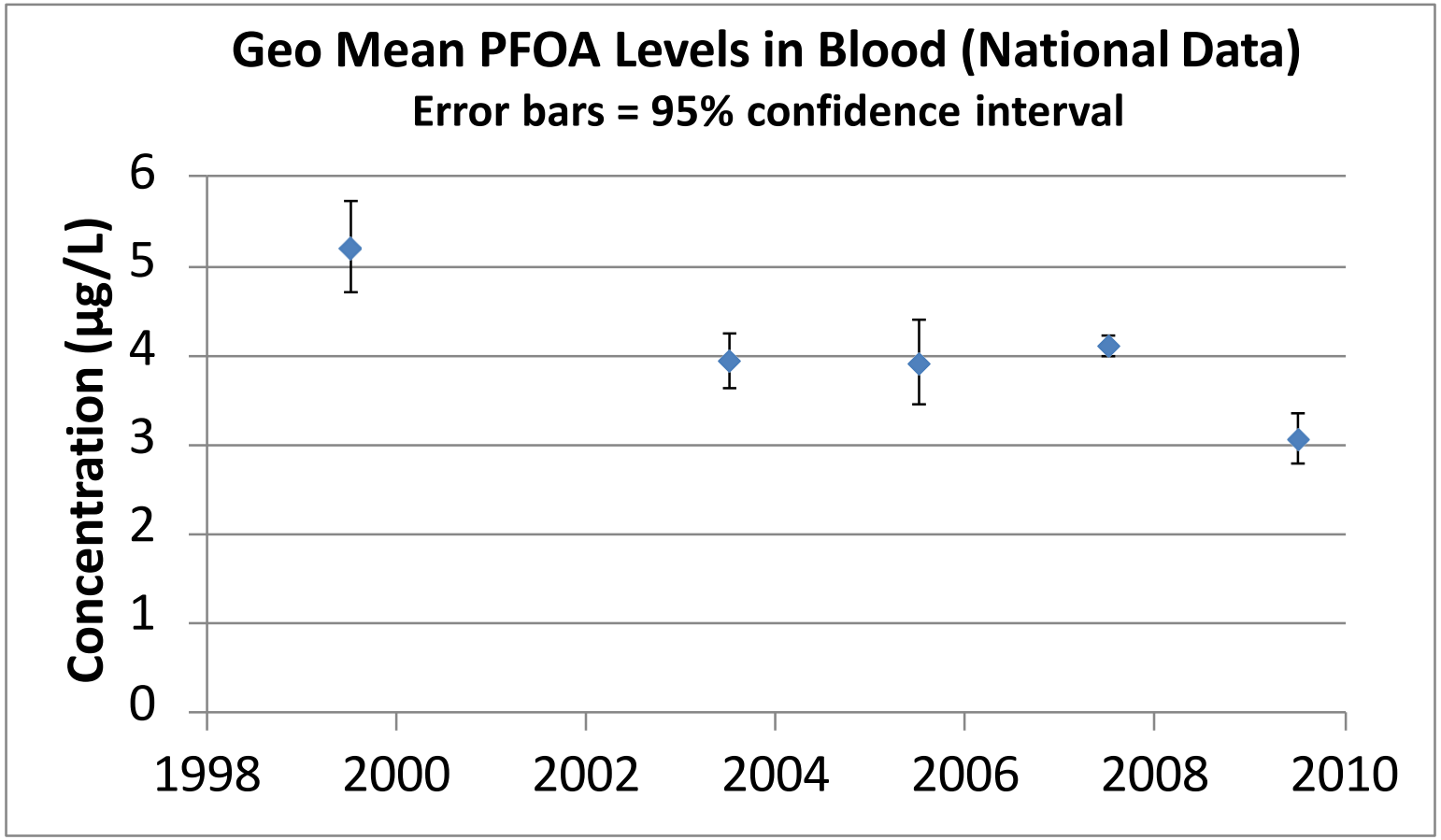
EPA, 2016

Developmental Exposures (Prenatal & Early Life)

- Of concern because **early life effects are sensitive endpoints** for PFOA toxicity.
- Found in human amniotic fluid, umbilical cord blood, and breast milk.
- Serum levels in infants
  - At birth, similar to maternal serum levels.
  - **Increase several fold during first few months of life.**
- **Exposures in infants are much higher than in older individuals.**
  - From breast milk or formula prepared with contaminated water.
  - Breast milk concentrations similar or higher than in maternal drinking water.
  - Consume more fluid per body weight.

PFOA in Blood in U.S. Population

NHANES data http://www.cdc.gov/biomonitoring/pdf/FourthReport_UpdatedTables_Feb2015.pdf

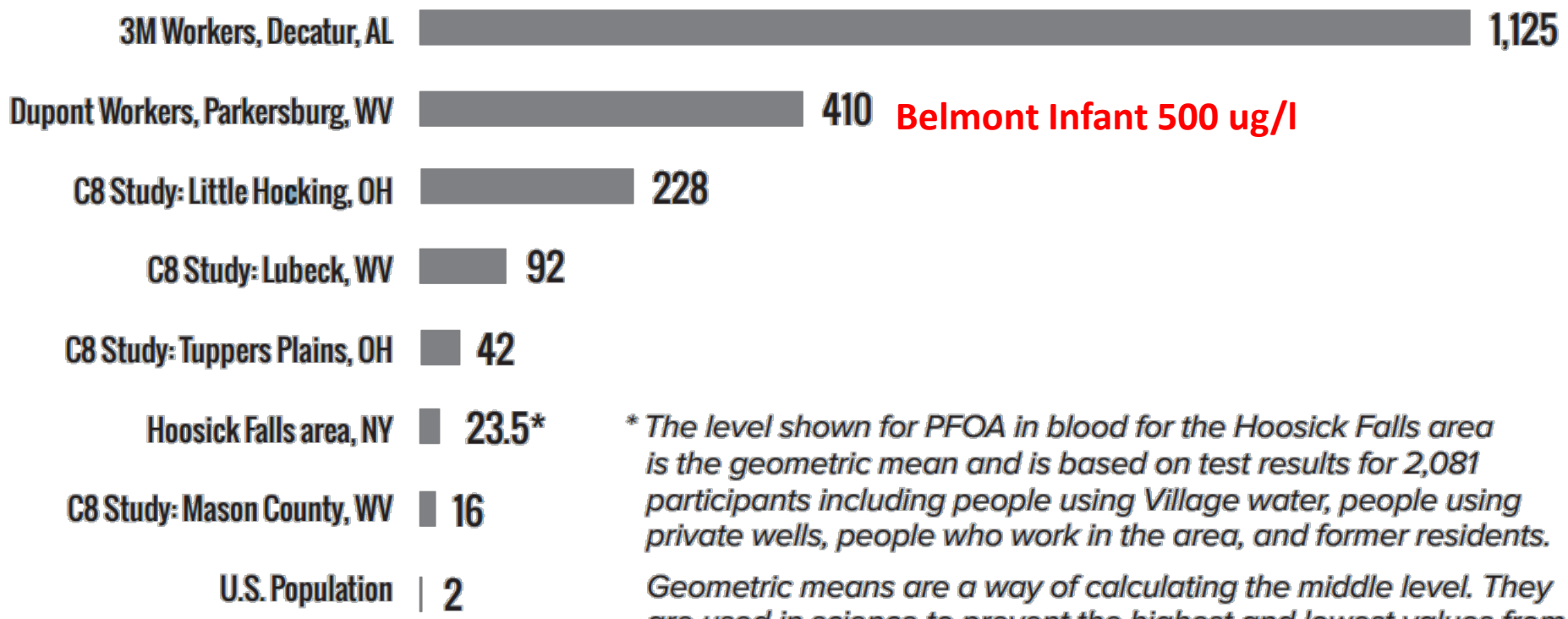


Current level ~2 µg/L (ppb)

Average PFOA Levels in Blood (µg/L)

(https://www.health.ny.gov/environmental/investigations/hoosick/docs/qandabloodtestingshort.pdf)

Belmont Resident 2,000 ug/l



Belmont Infant 500 ug/l

** The level shown for PFOA in blood for the Hoosick Falls area is the geometric mean and is based on test results for 2,081 participants including people using Village water, people using private wells, people who work in the area, and former residents.*

Geometric means are a way of calculating the middle level. They are used in science to prevent the highest and lowest values from distorting the average when rest of the data are close together.

PFAS in Drinking Water & Blood Serum

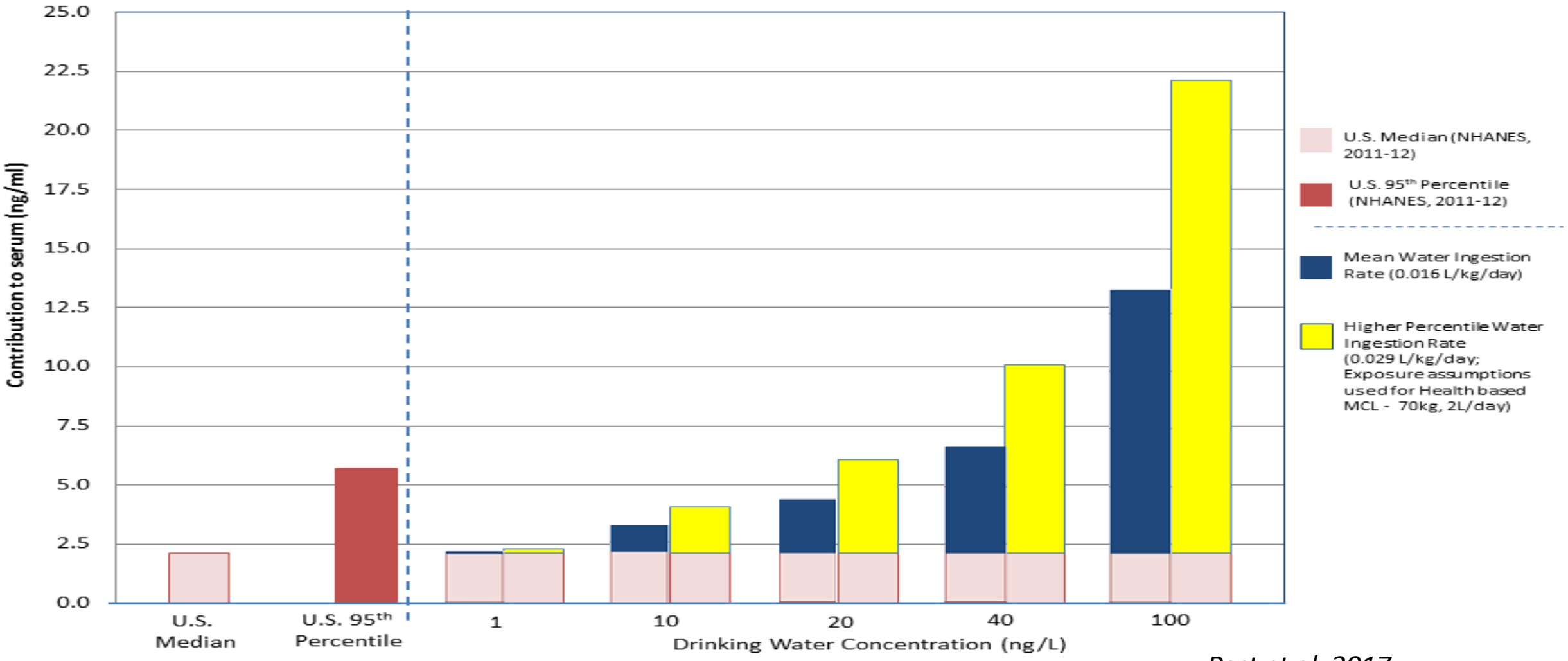
- Elevated PFAS levels in water ⇒ increased PFAS in blood
- Typical ratios (Braun, 2016 NEWMOA webinar)
  - PFOA: 125 µg/l (blood serum) / µg/l (drinking water)
  - PFOS: 175 µg/l (blood serum) / µg/l (drinking water)

Monitored PFOA Ratios in Blood Serum to Drinking Water
(Braun, 2016 NEWMOA webinar)

Study	N	Location	Water Source	Median
Emmett et al. 2006	291	Parkersburg, WV	Public/Private	105
Hoffman et al. 2011	108	Parkersburg, WV	Private	142
Hoffman et al. 2011	N/A	PK model	N/A	114
Hurley et al. 2016	1,566	California	Public	145

Ratio of 150 means 10 ppt in water => 1.5 µg/l in blood

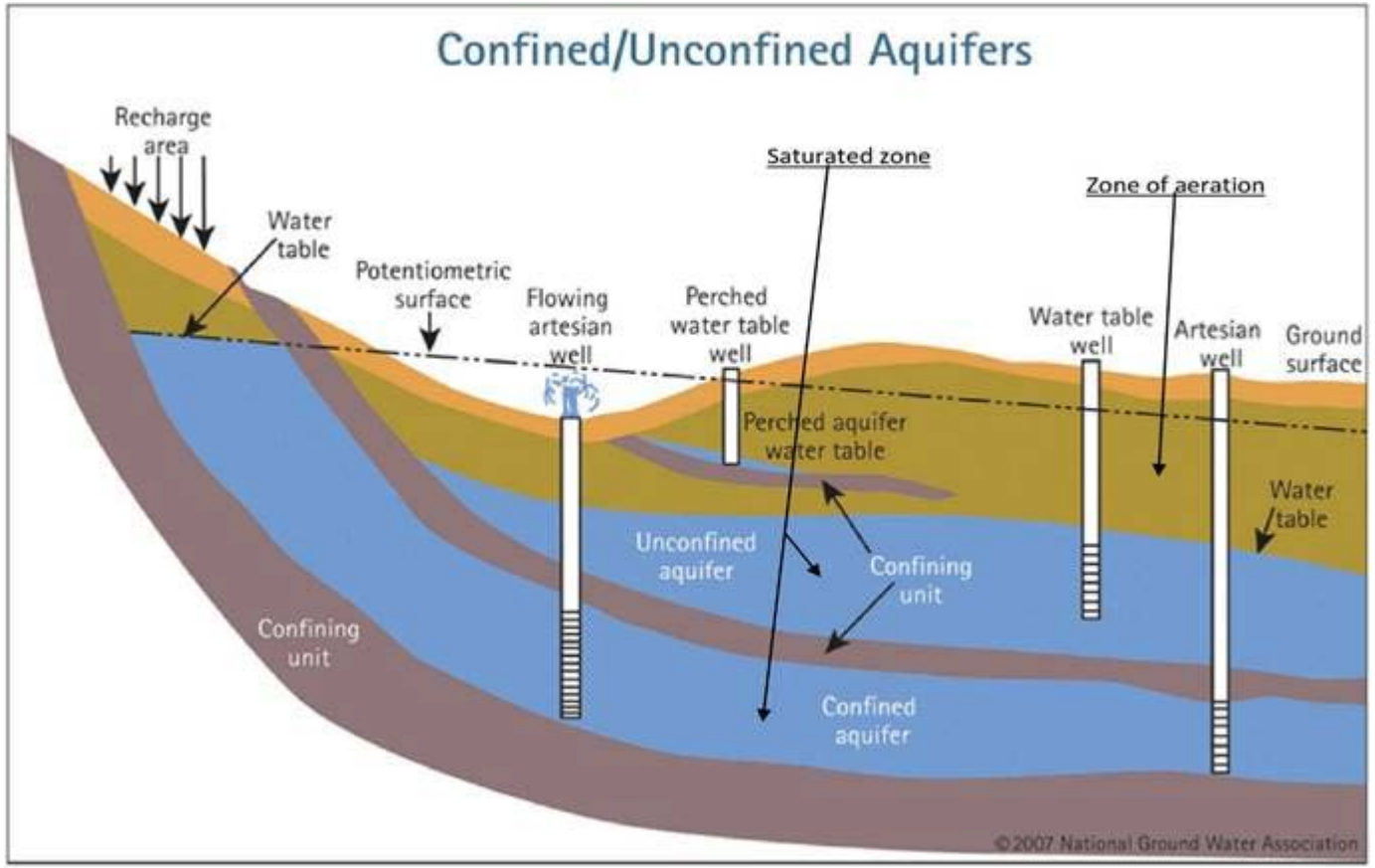
Increases in Serum Concentrations Predicted from Ongoing Exposure to PFOA in Drinking Water



Post et al, 2017

Groundwater Contamination Basics

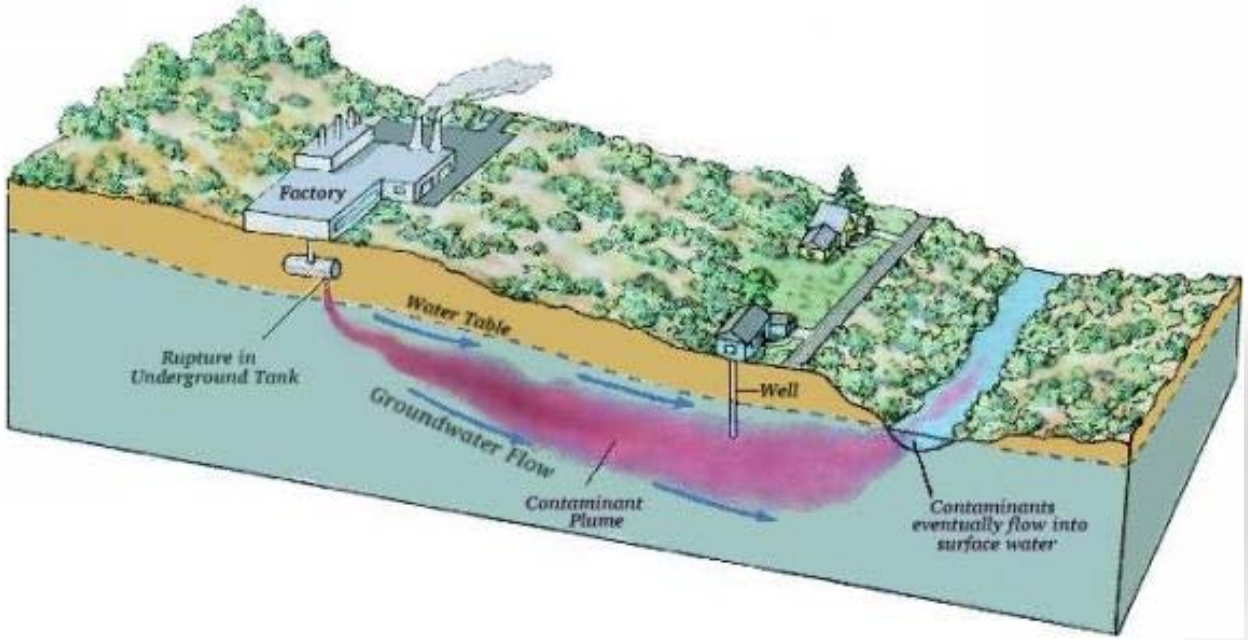
- Confined or unconfined aquifer

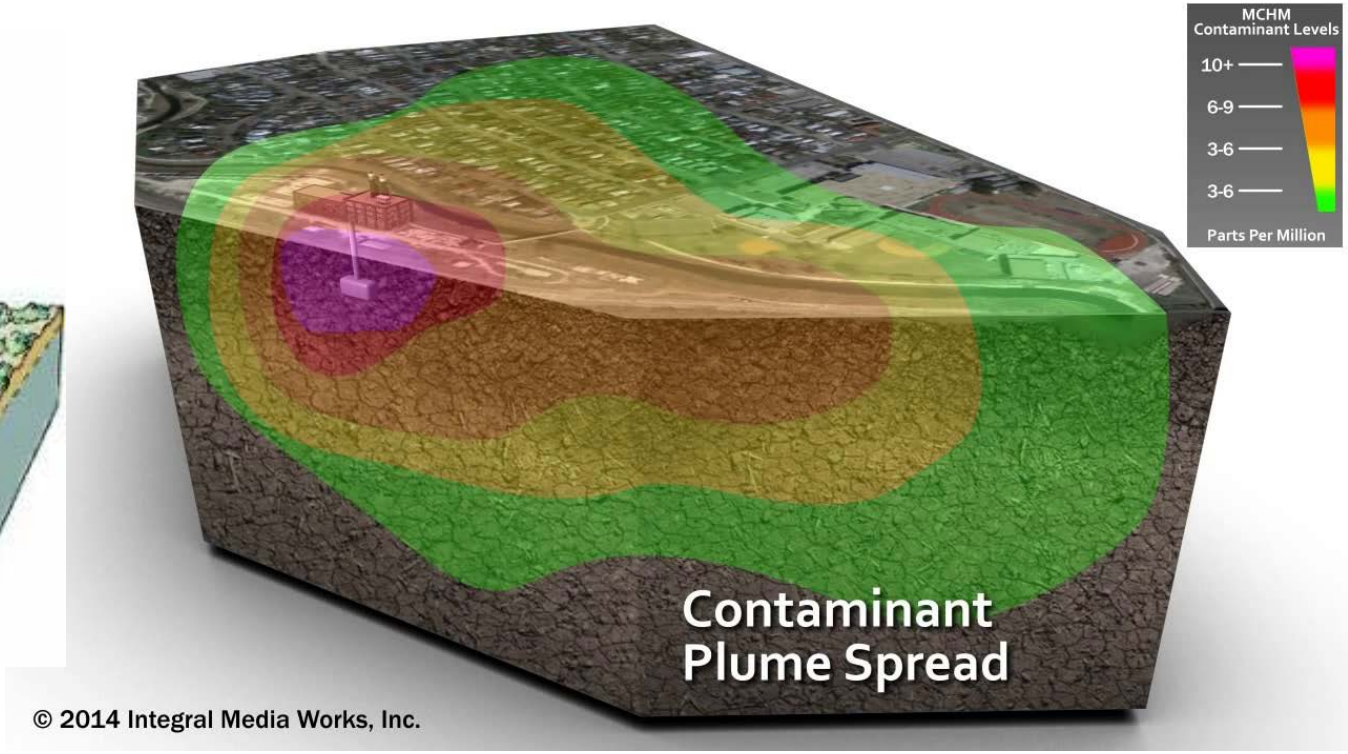


https://www.g-mwater.com.au/downloads/gmw/Groundwater/29012016-_2977263-v9-GROUNDWATER_TERMS_AND_DEFINITIONS_GLOSSARY_FOR_USERS.pdf

Groundwater Contamination Basics

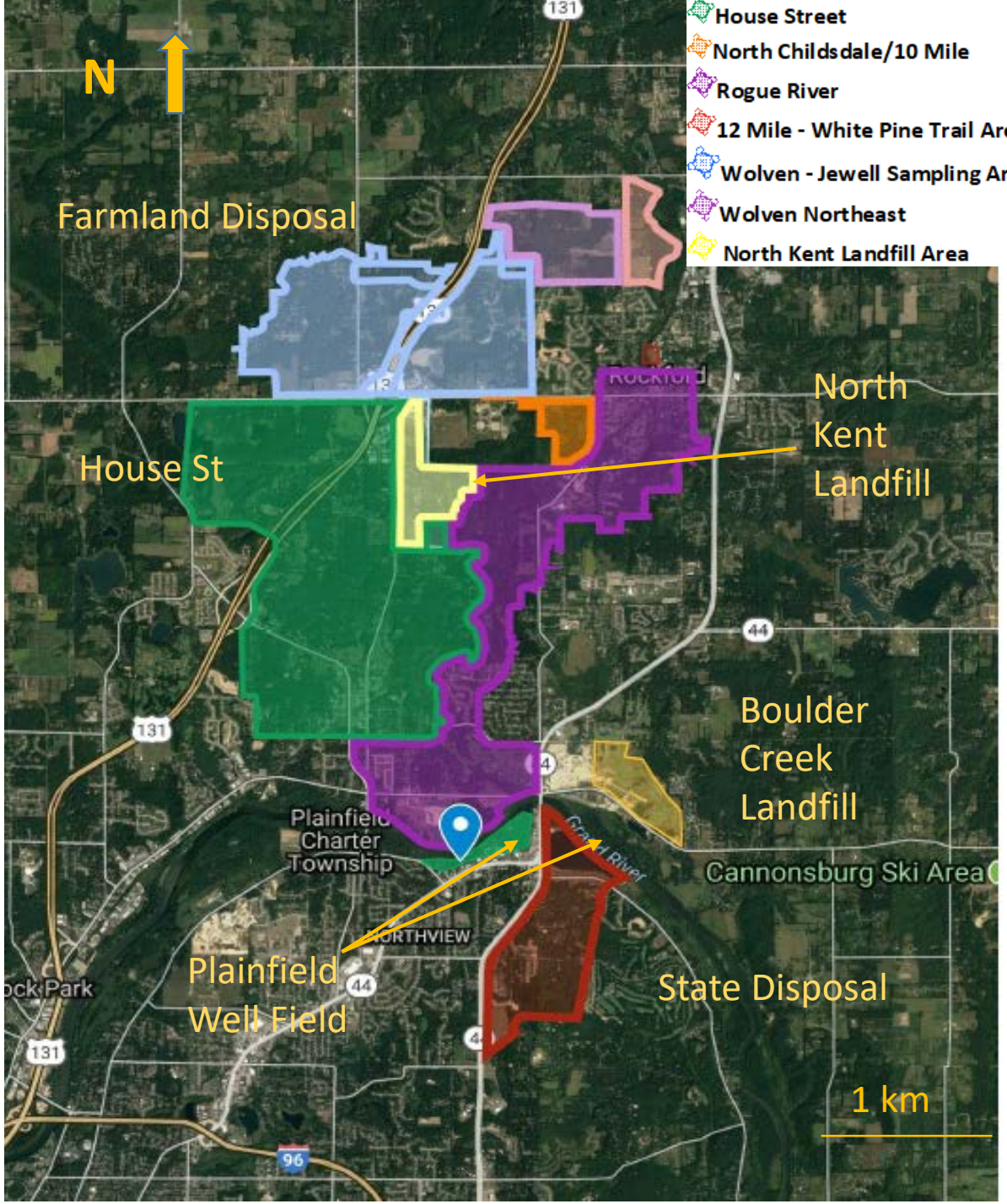
- Plume





http://geochico.csuchico.edu/mobile/ChicoToxicPlumes/

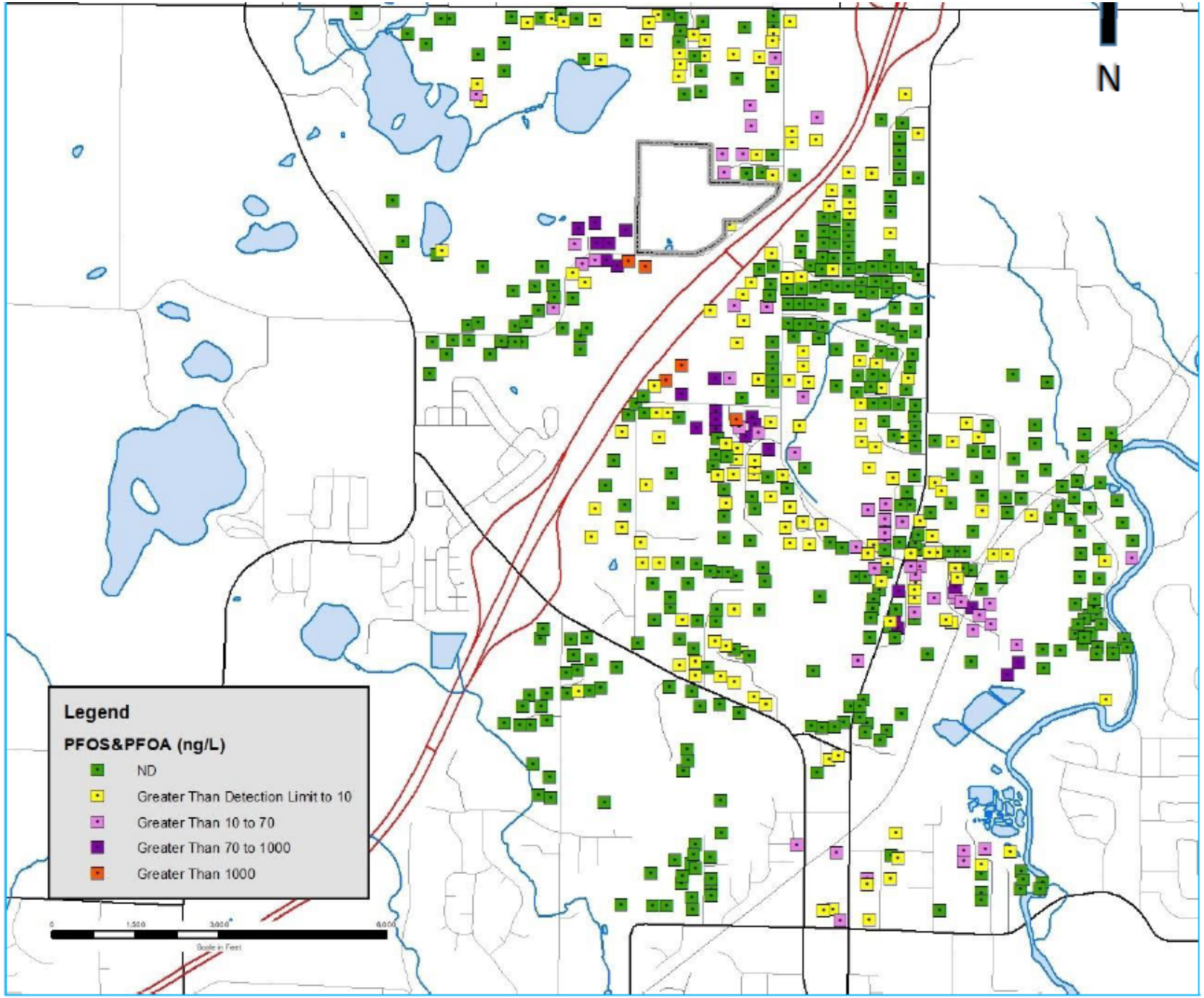
https://www.youtube.com/watch?v=Tv8imh0_bn4



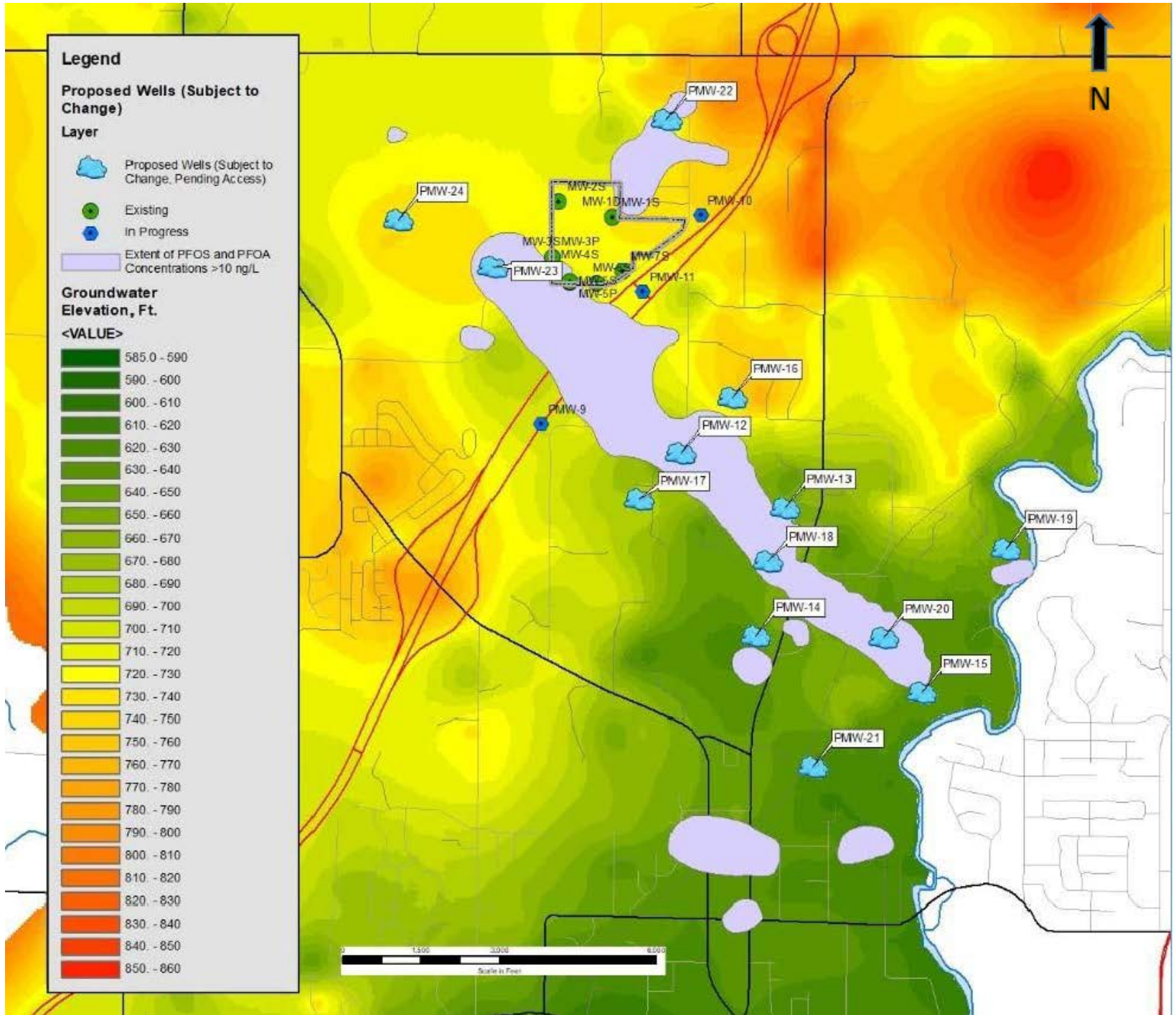
Rockford Area Plume

- Over 50 km^2
- Rogue River affected up to Sparta 40 km
- Waste disposal sites, landfills, gravel pits, the Tannery, and farmland disposal of sludge
- Plainfield township groundwater supply wells 40,000 people
- Thousands of residential groundwater wells

C. Angell, 2018


N
Legend
PFOS&PFOA (ng/L)
ND
Greater Than Detection Limit to 10
Greater Than 10 to 70
Greater Than 70 to 1000
Greater Than 1000
0
1,500
3,000
6,000
Scale in Feet

GZA, 2017


Legend
Proposed Wells (Subject to Change)
Layer
Proposed Wells (Subject to Change, Pending Access)
Existing
In Progress
Extent of PFOS and PFOA Concentrations >10 ng/L
Groundwater Elevation, Ft.
<VALUE>
585.0 - 590
590. - 600
600. - 610
610. - 620
620. - 630
630. - 640
640. - 650
650. - 660
660. - 670
670. - 680
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PMW-22
PMW-24
MW-2S
MW-1D
MW-1S
PMW-10
MW-3S
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MW-4S
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PMW-11
MW-5P
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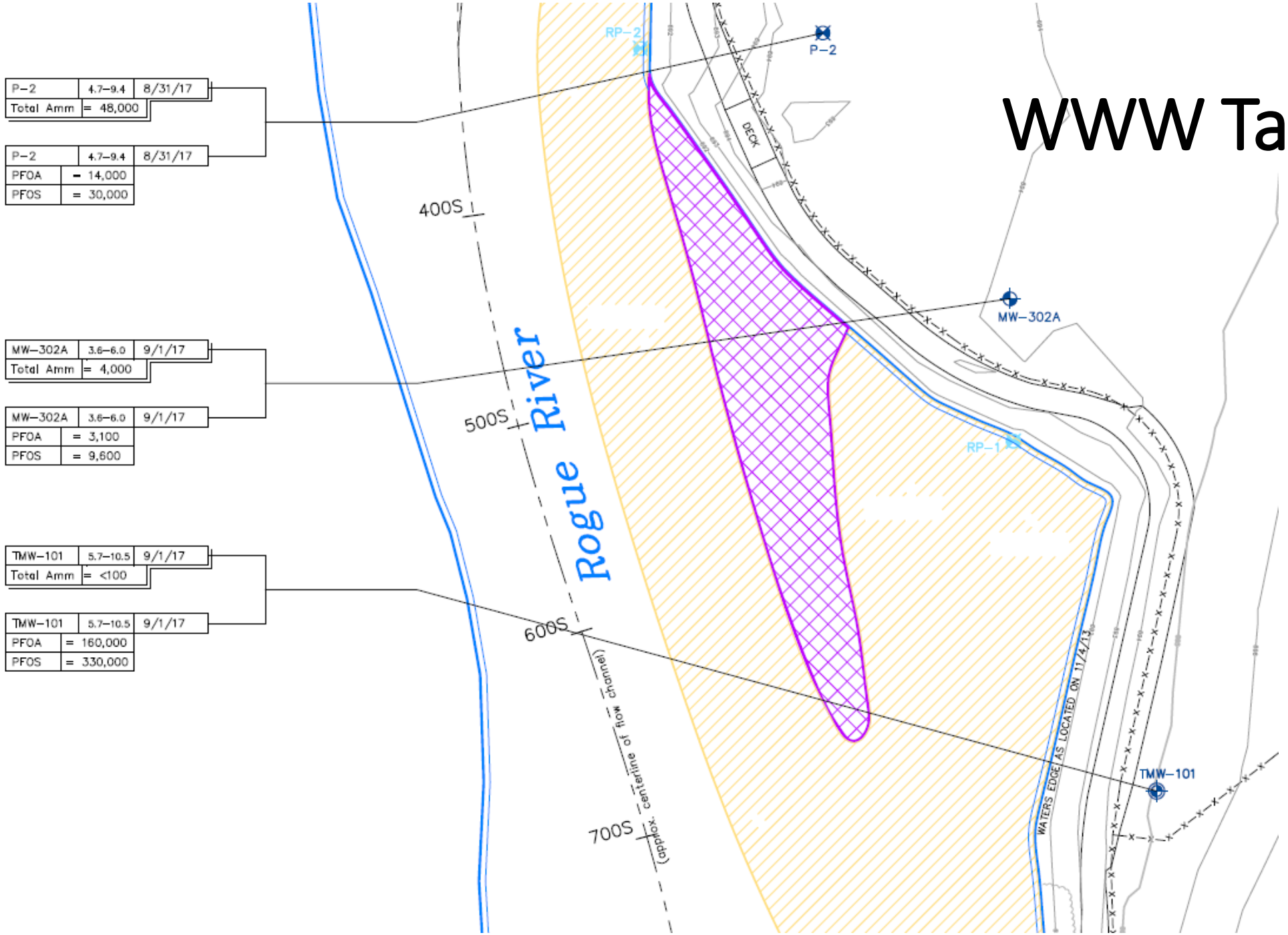
GZA, 2017

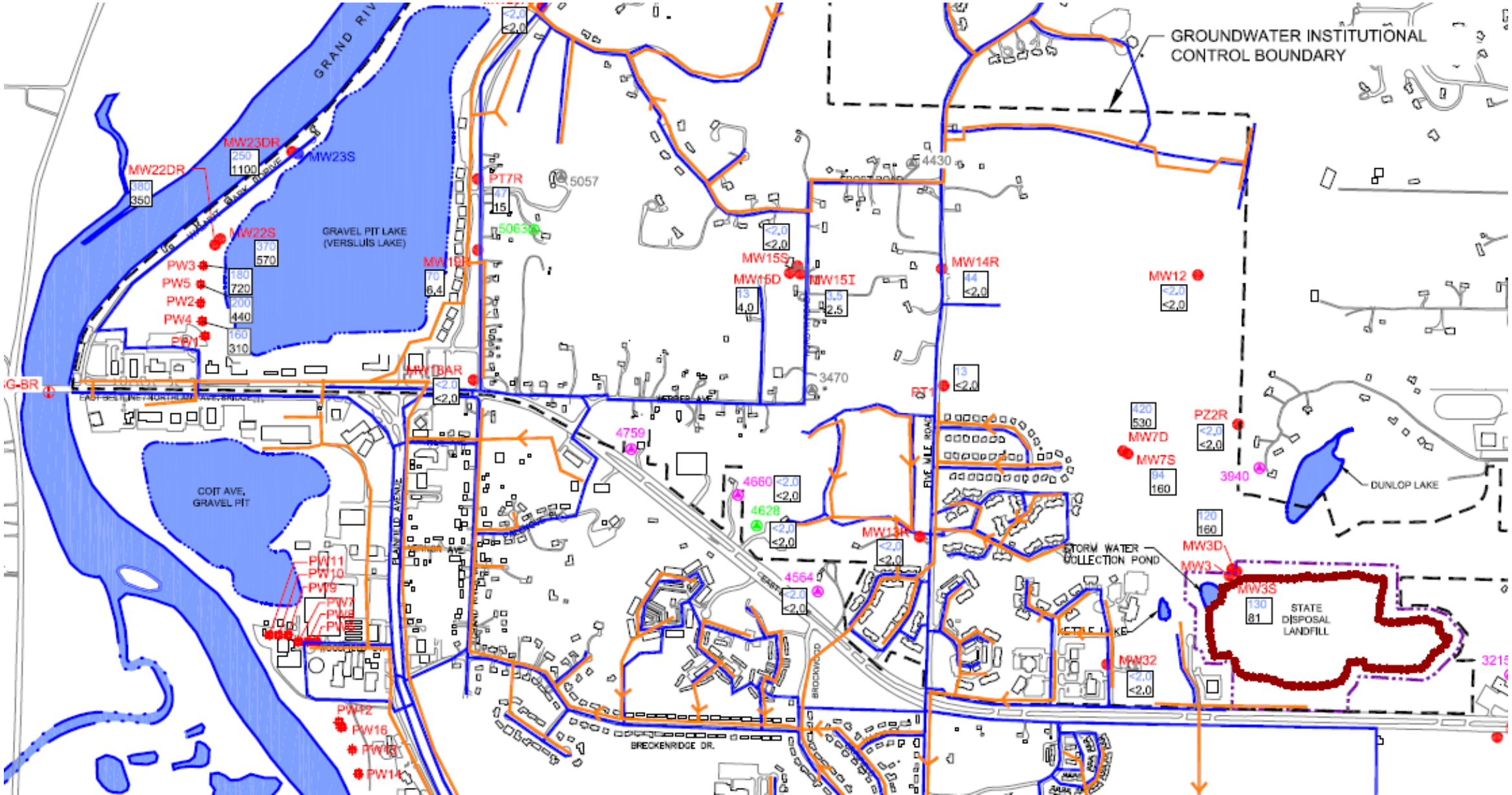
WWW Tannery



GZA, 2017

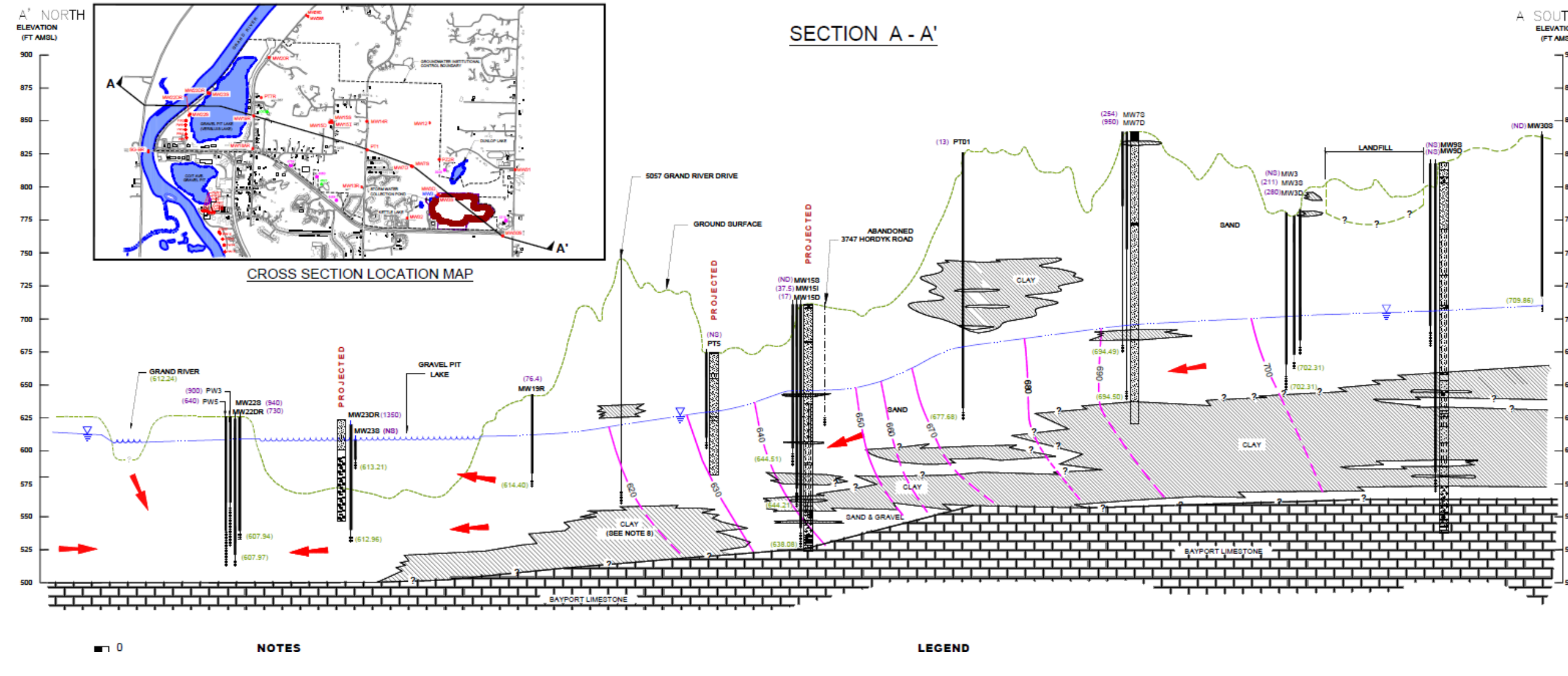
Plainfield Township Wells

(Waste Management 2017)



Plainfield Township Cross Section

(Waste Management 2017)



Home Drinking Water Treatment

- **Granular Activated Carbon Filters**
- https://www.michigan.gov/documents/deq/deq-dwmad-eh-swpu-FilterFactSheet_610096_7.pdf
- Aquasana, Culligan, and eSpring have NSF P473 Approved Carbon Filters
- Tap filters for low levels
- Whole House Filters for high levels
- All need testing to verify performance

Next Steps

- Area Wide Groundwater Assessment – USGS
- Expanded Epidemiology Study with Blood Testing (City of Rockford, Plainfield Township, Residents with Contaminated Wells
- Expand Study of Fish and Invertebrates in the Rogue River
- Public Outreach and Participation – Public Advisory Council
- GVSU Involvement - Public Advisory Council Steering Committee