Investigating Drinking Water Contamination in Ohio by Per- and Polyfluoroalkyl Substances

Jeff Patzke
Ohio EPA – Division of Drinking and Ground Waters
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Per- and Polyfluoroalkyl Substances (PFAS)

- A broad family of synthetic organic chemicals first developed by 3M in the late 1940s and used worldwide since the 1950s

- Some use “perfluorinated chemicals” or “PFCs”, but “PFAS” is what U.S. EPA prefers. PFCs doesn’t cover all of the chemicals of concern, so technically the term is not as broad.

- The most common specific PFAS are PFOS and PFOA

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PFAS are Emerging Contaminants

Defined as:

- Contaminants for which there is new awareness or understanding about how they move in the environment or affect public health, or
- Contaminants with known or potentially unacceptable risks to human health or the environment, and either:
  - There are no regulatory standards, or
  - The regulatory standards are evolving due to new science, detection capabilities, or pathways

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PFAS Then

2001 - Interest began when the contamination at DuPont's Washington Works plant was discovered. At that time:

- Labs could not detect low levels.
- Science suggested that low levels were not a health concern, and
- No routine testing in drinking water.

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PFAS Today

- Today – Better understanding of:
  - Persistence
  - Bioaccumulation
  - Toxicity
  - Widespread occurrence in ground, surface, and drinking water
- Can measure at parts per trillion level.
- Knowledge is rapidly evolving, but more work is needed.
- Still no routine testing of drinking water.

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Part I – PFAS 101

First half will cover general information, including:

- Unique properties of PFAS
- Widespread application in industry and manufacturing
- Persistent and widespread occurrence in environment
- Human exposure and health effects
- U.S. EPA efforts to phase out and replace
- Occurrence in drinking water – current safe levels and treatment methods

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Part 2 – Investigating Drinking Water Contamination by PFAS

Get more specific on the Ohio Issues that we know about

What is Ohio EPA doing to find out if there are more issues?

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Per-and Polyfluoroalkyl Substances (PFAS)

- Class includes polymers and non-polymers
- Today's focus is on non-polymers
- All molecules contain C and F, and may also include O, H, S, and/or N
- All molecules are C chains with at least one C-F bond, and at least one H replaced by a non-H atom or molecule
- Many chemicals exist in various states as acids, anions, or cations.
- Two main non-polymer groups:
  - Per-
  - Poly-

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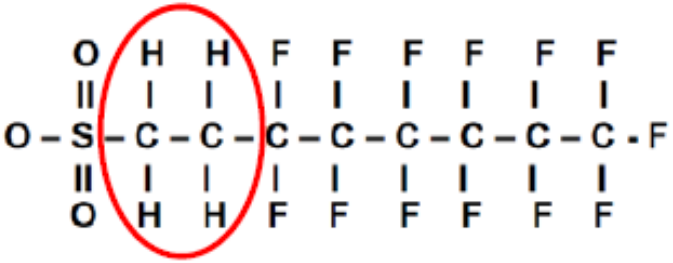
Polyfluoroalkyl Substances



- Have not gotten as much attention
- Molecules have a non-F atom, usually H or O, attached to at least one, but not all, C atoms, while at least two or more of the remaining C atoms have F attached
- So molecules are “not fully fluorinated”
- Bonds with non-F atoms are weaker and subject to degradation
- This is why poly-substances can be a precursor to per- substances

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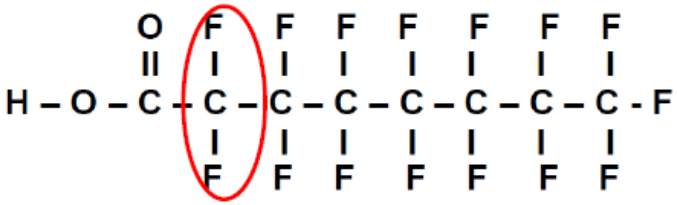
Perfluoroalkyl Substances



Perfluoro-octanoic Acid (PFOA)

- Perfluoroalkyl substances are fully fluorinated -all C atoms have an attached F atom, except where the acid head is attached
- There is a chain (tail) and an acid (head)
- Concerned with perfluoroalkyl acids (PFAAs) because they have been found in drinking water and can cause health effects
- Especially concerned with long-chain PFAAs because they are more persistent, bioaccumulative, and toxic
- Long-chain means eight or more Cs when the acid is carboxylic, and six or more when the acid is sulfonic

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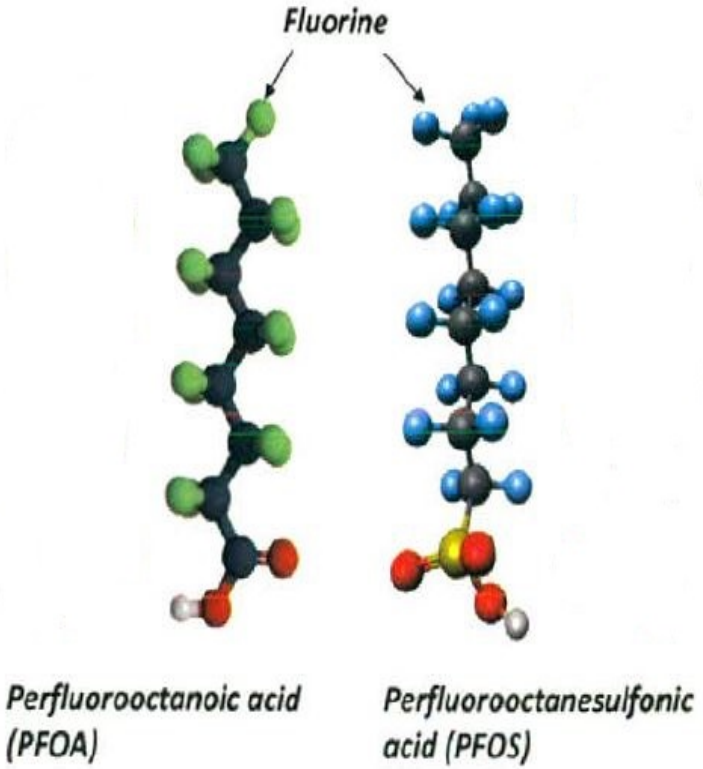
PFOS and PFOA



- Two long-chain PFAS, both with 8Cs, have gotten the most attention
- Typically occur in the environment as anions, and they form from the degradation of many other PFAS

	Acid	Anion
PFOS	Perfluorooctane Sulfonic Acid $C_8F_{17}SO_3H$	Perfluorooctane Sulfonate $C_8F_{17}SO_3^-$
PFOA	Perfluorooctanoic Acid $C_7F_{15}COOH$	Perfluorooctanoate $C_7F_{15}COO^-$

These are the PFAS that are most studied and produced.

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PFAS Chemical Properties

- Dictate use in industry/manufacturing and how they behave in the environment
- Molecules are hydrophobic and lipophobic
- Very resistant to hydrolysis, oxidation, and reduction because:
  - The C-F bond is the strongest in organic chemistry
  - High electronegativity of F atoms
  - The small size and dense packing of F atoms shield the C backbone

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PFAS Uses

Industry

- Many are used as surfactants
- They reduce friction, and are used in industries such as aerospace, automotive, construction, and electronics

Consumer Products

- Non-stick cookware and food packaging
- Soil-, stain-, water-resistant materials in homes, shoes, and clothing

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Fire Fighting Foams

- Aqueous film forming foam (AFFF) for fighting petroleum-based fires
- These are called Class B Foams
- Rapidly forms a film across the fire surface, which prevents the release of flammable fuel vapors and excludes oxygen

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PFAS Sources

PFAS are widespread in the environment

Major Sources:

- Industrial releases,
- Use of AFFF,
- Disposal of industrial and consumer waste, and
- Wastewater treatment plants/biosolids

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PFAS Occurrence in the Environment

- In soil, sediments, air, oceans, rivers, lakes, ground water, and precipitation
- In ground water, large plumes can form due to low sorption and high solubility
- In tissues of humans, animals, birds, fish, and invertebrates throughout the world
- PFAS are probably being transported by long-range atmospheric and oceanic currents

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PFAS Contamination by Air Deposition

Some industrial processes can release PFAS into the air, so you can see contamination over a large area

Ground water can become contaminated around facilities that produce, manipulate, or apply fluorinated coatings or products.

Happens when fluorinated coatings are prepared from colloidal aqueous dispersions of polytetrafluoroethylene (PTFE) particles that are stabilized with surfactants, such as PFOS and PFOA.

The surfactants are removed by drying, and PFOA and PFOS are emitted from stacks.

Source: NGWA(2018)

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PFAS Persistence

- Very persistent because they resist degradation
- Acids like PFOS and PFOA are “terminal degradation products”, meaning no further products will form:
  - Are essentially non-degradable
  - Bioaccumulate – long-chain PFAS have half-lives of 2-9 years
  - Are highly soluble and mobile, so can get into drinking water easily (unlike PCBs and dioxins)

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$UCMR_3$ Sampling Results

Sampling U.S. EPA required under Unregulated Contaminant Monitoring Rule (2013-2015)

Purpose: Provide information to evaluate unregulated chemicals for possible regulation

Finished water collected: At all PWSs serving >10,000 and some <10,000

Results: PFOS/PFOA detected at 4% PWSs

EPA Health Advisory Level exceeded at 1%

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Exposure

Blood Levels

- Most people have measurable PFAS in their blood
- Detection frequency and levels are higher than for other environmental contaminants
- The levels reflect exposure over many years
- Average levels are 2.1 ppb for PFOA and 6.3 ppb for PFOS (CDC, 2012)
- Levels appear to be decreasing due to phase-out

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Exposure

Drinking Water

- One of the most potent ways for people to be exposed to PFAS
- Drinking includes using water for cooking, baby formula, and teeth brushing uses
- Even low concentrations can substantially increase blood levels, but they decrease slowly when the exposure is eliminated
- Using PFAS-contaminated water is not a concern for showering and dish washing

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Exposure

Food

- Primary PFAS exposure route for most people
- Food can become contaminated:
  - Fish from contaminated surface water
  - Fruits and vegetables from contaminated soil or irrigation water
  - From packaging (e.g. grease-resistant paper)
- According to U.S. EPA cooking with Teflon-coated pans is not considered to be a concern.

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Exposure

Consumer Products

- Potential for exposure to PFAS is relatively low compared to drinking water and food

Stain-Repellent, Water-Repellent, or Non-Sticky	Other	
Carpets Leather Clothing Paper Packaging Ski Wax	Cleaning Products Adhesives Fabric Softeners Paints Dyes Inks	Auto Interiors Cosmetics Shampoo Dental Floss Toothpaste

- Because of consumer products, particularly carpeting, indoor air may contain PFAS that can be ingested
- But potential for exposure is lower today due to PFOS/PFOA phase-out

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Exposure

Outdoors

- Breathing contaminated dust – but outdoor PFAS concentrations in air are typically much less than indoor air
- Soil, snowmelt, surface waters near ski areas may have measurable PFAS because of ski wax
- Swimming is not likely to cause significant exposure

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Exposure

Occupational

- When PFAS are manufactured, used to make things, or used in industrial processes
- Also when products with PFAS are used, such ski wax, firefighting foams, aviation fluids, lubricants, surfactants, and emulsifiers
- Exposure is typically by inhalation or ingestion, and it is at levels that are far greater than for the general public

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Health Effects

- Toxicity data is lacking for many PFAS
- Most studies are based on PFOA and PFOS
- Potentially an increased risk of testicular and kidney cancer, as well as:
  - Changes in cholesterol
  - Effects to fetuses or breastfed infants
  - Liver, thyroid and immune system effects

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PFOS/PFOA Phase-Out

- Both chemicals, as well as a number of related chemicals, are no longer manufactured in the U.S., due to U.S. EPA rules and voluntary actions.
- U.S. EPA has required use of PFOS as a fume suppressant in the chromium electroplating industry to be phased out
- In January 2016, FDA has ceased allowing PFOS/PFOA in food packaging
- U.S. EPA also required better reporting on new use of PFOA in carpets and import of carpets with PFOA

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What It Means

Although PFOA and PFOS are no longer manufactured in the U.S., they are still produced elsewhere, and they continue to be in imported goods.

Environmental contamination is expected to continue due to:

- Persistence
- Continued formation of precursors
- Ongoing production by non-participating manufacturers

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Replacement Chemicals

Goal: Find new substances that are less toxic and persistent with a focus on shorter-chain PFAs

Not easy, because:

- Chemical information is limited
- Many not detected by standard analytical methods

Gen-X: Short-chain PFAS approved for use by Chemours in Fayetteville, NC

- Commercially produced, but also a byproduct
- Health effect information is limited
- Thought to leave body more quickly than PFOA, but is more difficult to treat in drinking water
- No federal health guidelines, but are under development

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DuPont/Chemours

- Replaced PFOA with Gen-X at Fayetteville, NC plant in 2009
- Contamination concerns:
  - 115 private well owners receiving bottled water
  - Gen-X found in rainwater at up to 630 ppt
- NC DHHS:
  - Requiring Chemours to eliminate or reduce emissions
  - Set drinking water health goal at 140 ppt
- U.S. EPA: considering reevaluating original risk assessment for pre-market approval

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Drinking Water Health Advisories

- Currently no federal MCLs for PFOS/PFOA
- U.S. EPA has set health advisory levels (HALs) for PFOS/PFOA
- U.S. EPA is partnering with the National Toxicology Program to quickly generate toxicity and kinetic information for about 75 PFAS
- The 75 compounds were selected to represent all PFAS based on occurrence in the environment, diversity of chemical structures, volatility, and solubility

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Lifetime HAL

- 2016 – Replaced temporary or "provisional" HALs (2009) with one lifetime HAL of 70 ppt, which is a combined level for both PFOS/PFOA
- The lifetime HAL:
  - Is advisory and not legally enforceable
  - Provides PWS operators with information on health risks so they can take appropriate action
  - Offers a margin of protection for all Americans throughout their lives, from adverse health effects, including:
    - Developmental effects to fetuses or to breastfed infants
    - Cancer (e.g., testicular, kidney)
    - Liver, immune system, thyroid, and other effects
  - Applies only to drinking or water used for food preparation
  - Non-drinking water exposure was accounted for in the development
- Many PWSs with water >70 ppt under UCMR have acted to reduce levels including shutting down wells, blending water from different wells, and treating the water

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Differences in State Safe DW Levels

Levels implemented vary across states (ppt):

- OH, MI: 70 combined PFOS/PFOA
- MN: 35 (PFOA), 27 (PFOS)
- VT: 20 (PFOA)
- NJ MCLs: 14 (PFOA), 13 (PFNA), *draft* 13 (PFOS)

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U.S. EPA Regulatory Evaluation for PFOS/PFOA

MCL would provide more certainty and consistency.

Would be a determination under these SDWA criteria:

- May have adverse health effects to people
- Known or likely to occur in public water systems with frequency and levels sufficiently high to be a public health concern
- Regulation presents a meaningful opportunity for health risk reduction.

UCMR data from 2013-2015 are being considered.

EPA must decide whether or not to regulate at least five candidates that were listed in 2016 by January 2021.

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Treatment

- Many conventional treatment techniques are not effective at removing PFAS
- Same properties that make PFAS persistent in the environment and valuable in industry can make treatment difficult
- For example, the strong C-F bond and low vapor pressure means that some are resistant to oxidation, biodegradation, and air stripping
- Three methods can be effective

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Granulated Activated Carbon

- GAC: Water is run through filters to trap or adsorb dissolved PFAS
- Sometimes known as “charcoal filters” because heat has been used to increase the surface area of the carbon
- Most effective for long-chain PFAS; short-chain PFAS are more soluble
- No concentrated waste streams are generated that need to be disposed
- GAC filter needs to be changed when it can no longer remove chemicals

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Reverse Osmosis

RO: Water is pushed through a semi-permeable membrane

Chemicals too large to pass are held back

Disadvantage: Waste stream with high PFAS is generated that could be up to 30% of the volume treated

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Anion Exchange

Anion Exchange: Water is run through resins with a fixed charge, and contaminant ions are exchanged with hydrogen or hydroxyl ions

Whether there is a waste stream depends on the type of system

WRF: Anion exchange is highly effective for PFOS, moderately effective for PFOA, and ineffective for some other PFAS

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Home Treatment

Home filtration systems employing GAC or RO are available, including:

- Point-of-use (POU) systems that attach where water is dispersed
- Point-of-entry (POE) systems that are installed at a home's main waterline

NSF International developed a certification standard in 2016 for reducing PFOA and PFOS in water:

- A filter must be tested and meet ANSI requirements
- A filter must reduce levels to below U.S. EPA lifetime HAL

To date, NSF has certified some POU GAC and RO filters from three manufacturers.

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Known Ohio PFAS Contamination Sites

- DuPont/Chemours Washington Works Plant, Parkersburg, WV
- Newport Volunteer Fire Department
- Wright Patterson Air Force Base
- Dayton Fire Training Center
- Toledo Air National Guard Base

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DuPont/Chemours

- DuPont created Chemours in 2015 to handle production of Teflon and other chemicals
- PFOA (C-8) was used to make Teflon from 1951-2013, when it was replaced with Gen-X
- Facility has contaminated public and private drinking water in parts of Washington, Athens, and Meigs Counties in Ohio
- U.S. EPA has had the lead regulatory role

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Class Action Lawsuits

2005 – DuPont settled a $343 million class action for contaminating drinking water supplies in WV and Ohio with C-8 and causing health effects to the residents.

Also agreed to set up an independent panel to study links between C-8 exposure and human health problems (C-8 Health Project).

February 2017 – Chemours agreed to pay $671 million to people exposed to C-8

- Study found residents' blood (38 ppb median) was 7X average American
- Awards based on specific adverse health effect

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Ohio AGO Lawsuit

February 2018 – Ohio AGO sued Chemours for impacts to natural resources

Determine clean-up needed for soils, ground water and surface water

Implement clean-up

Purpose is to seek abatement of public nuisance rather than a set dollar amount

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Concealing C-8 Risk Information

2005 – DuPont agreed to pay $10.25 million to U.S. EPA for not reporting chemical risk information (largest environmental penalty at that time)

DuPont began using C-8 in 1951, considered it to be potentially toxic in 1954, and verified toxicity in 1961

Through the 70s, 80s, and 90s, DuPont came to understand that C-8 accumulated in the body and was getting into public drinking water

Purchased Lubeck, WV wellfield in 1988 for $2 million and paid for a new one two miles down river

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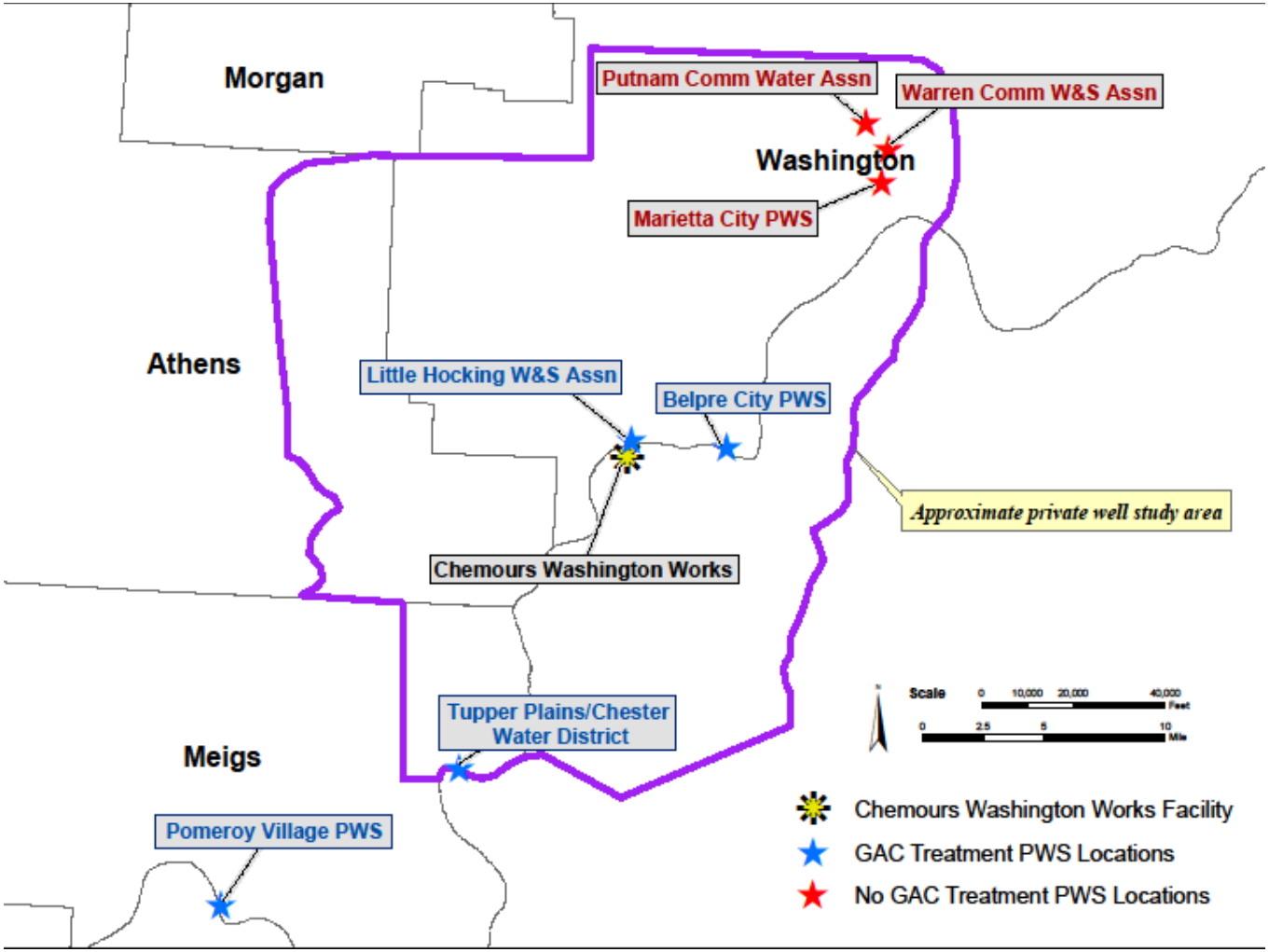
Drinking Water Sampling and Treatment



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Ohio River Water Systems (PFOA) with GAC Treatment

Little Hocking

- Raw water up to 22,000 ppt, historically; currently at 8,000 ppt
- GAC treatment is effective

Belpre

- Raw water currently 330-350 ppt
- GAC treatment is effective

Tupper Plains/Chester and Pomeroy

- Raw water typically <70 ppt; Pomeroy is ND

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Muskingum River
Public Water Systems

Marietta, Warren Community, and Putnam (Devola) all have raw water PFOA < 70 ppt

Chemours is not required to provide treatment if PFOA < 70 ppt

Putnam is close to 70 ppt; however, reverse osmosis for nitrate is reducing PFOA to < 20

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Ohio Private Well Sampling and Treatment

Area of about 440 mi^2

451 residential wells sampled since 2001, with PFOA detected in 346 and above 70 ppt in 240

Chemours is providing treatment for homes above 70 ppt, and has hooked others up to public water

GAC treatment has been effective

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PFOA Surface Water Contamination

Recent U.S. EPA/OSU study shows PFOA surface water contamination in the same general area where private wells are sampled

PFOA surface water levels:

- >1,000 ppt close to plant
- >100 ppt 15 miles away
- >10 up to 25 miles away

Indicates extensive soil and ground water contamination

Lower levels of Gen-X also found in surface water

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Drinking Water Gen-X Sampling

Results received March 2018

U.S. EPA Region 3 requested Gen-X sampling at two public wells and five private wells with the highest raw water PFOA

No Gen-X in finished water

Gen-X in all raw water except Belpre; levels were 30-50 ppt, below NC 140 ppt HAL

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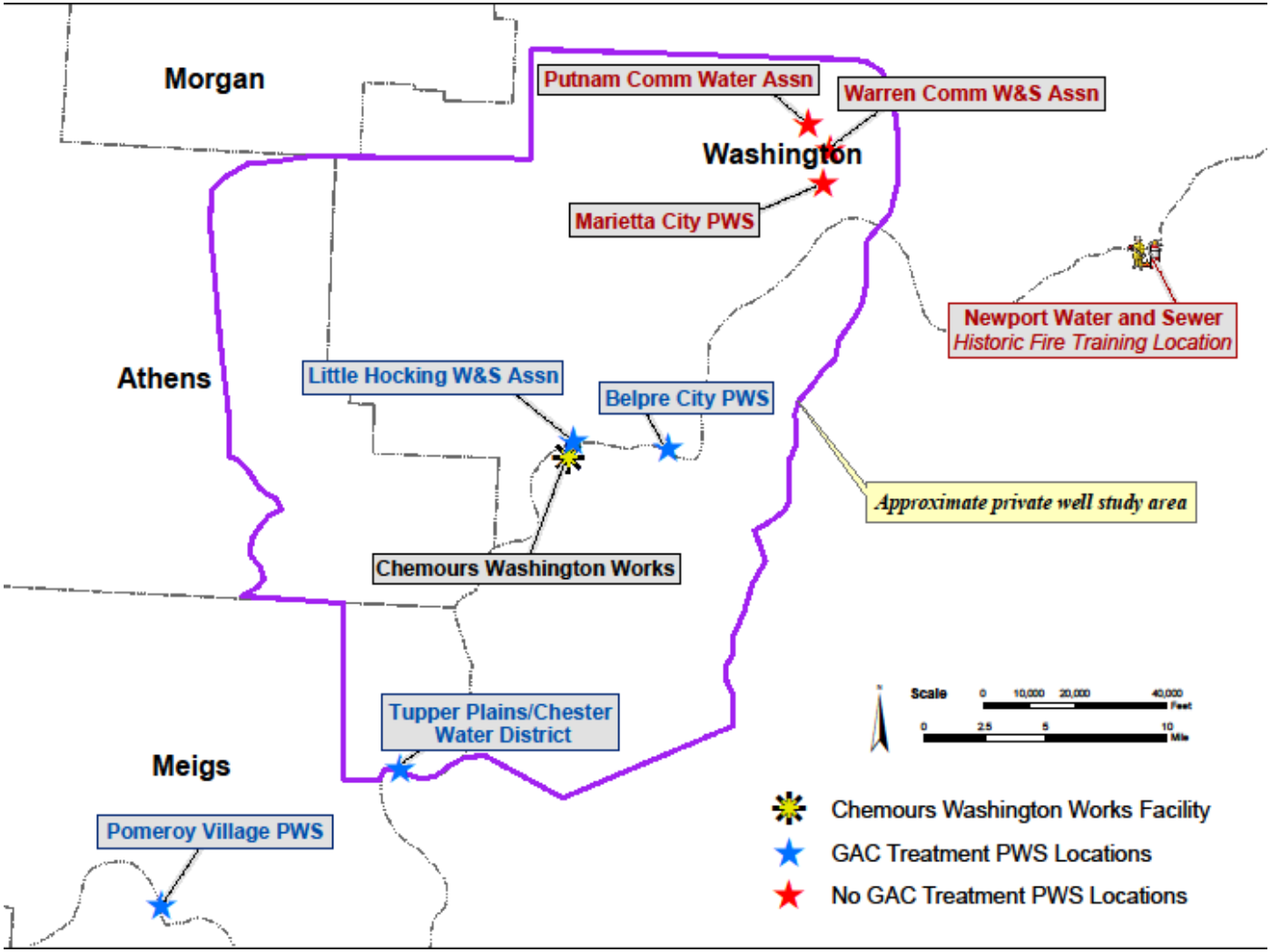
Ohio Drinking Water Sampling and Treatment



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Newport Volunteer Fire Department

Hosted fire training for southern Ohio fire depts. (1964-1974)

Extinguish fires produced using waste from industrial companies in the area (e.g., Union Carbide)

Newport Wellfield installed 1969, with PW-2 150’ from burn pits

VOC contamination found in PW-2 in 1986; PW-2 became a recovery well

Because of the historical use of AFFFs, Ohio EPA sampled for PFOS and PFOA in October 2016.

PFOS was detected in the recovery well (175 ppt), but not in the production well or finished water

Continued operation of the recovery well should prevent PFOS from getting into the PWS raw water

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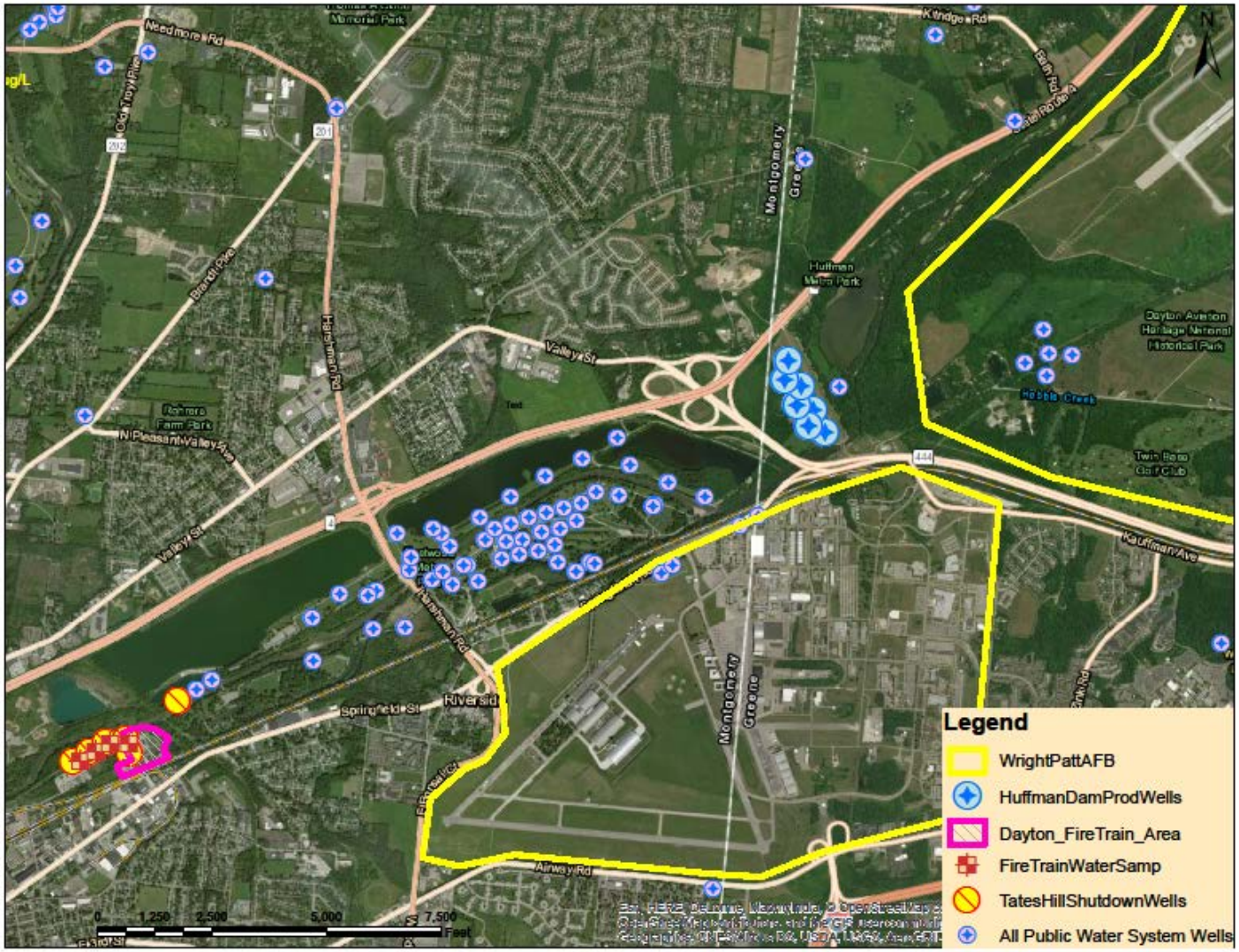
Fire Training Locations and Public Wells Northeast Dayton



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Wright Patterson AFB

Historical use and management of fire-fighting foams

Federal investigation defined soil and water contamination

PWS serves 16,500 on-base residents

May 2016- two wells that serve part of the base were shut down due to exceeding 70 ppt for PFOS and PFOA.

June 2017- Pumping of the two wells resumed after construction of a $2.7 million charcoal filtration plant.

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Huffman Dam Wells

Because of the PFAS contamination at WPAFB, seven Dayton PWS wells have been shut down since July 2016 as a precaution

Contamination has moved beyond the property boundary, but PFOS/PFOA levels off-base are well below 70 ppt

Ohio EPA and Dayton are urging action and better monitoring to prevent ground water in the wellfield from exceeding 70 ppt.

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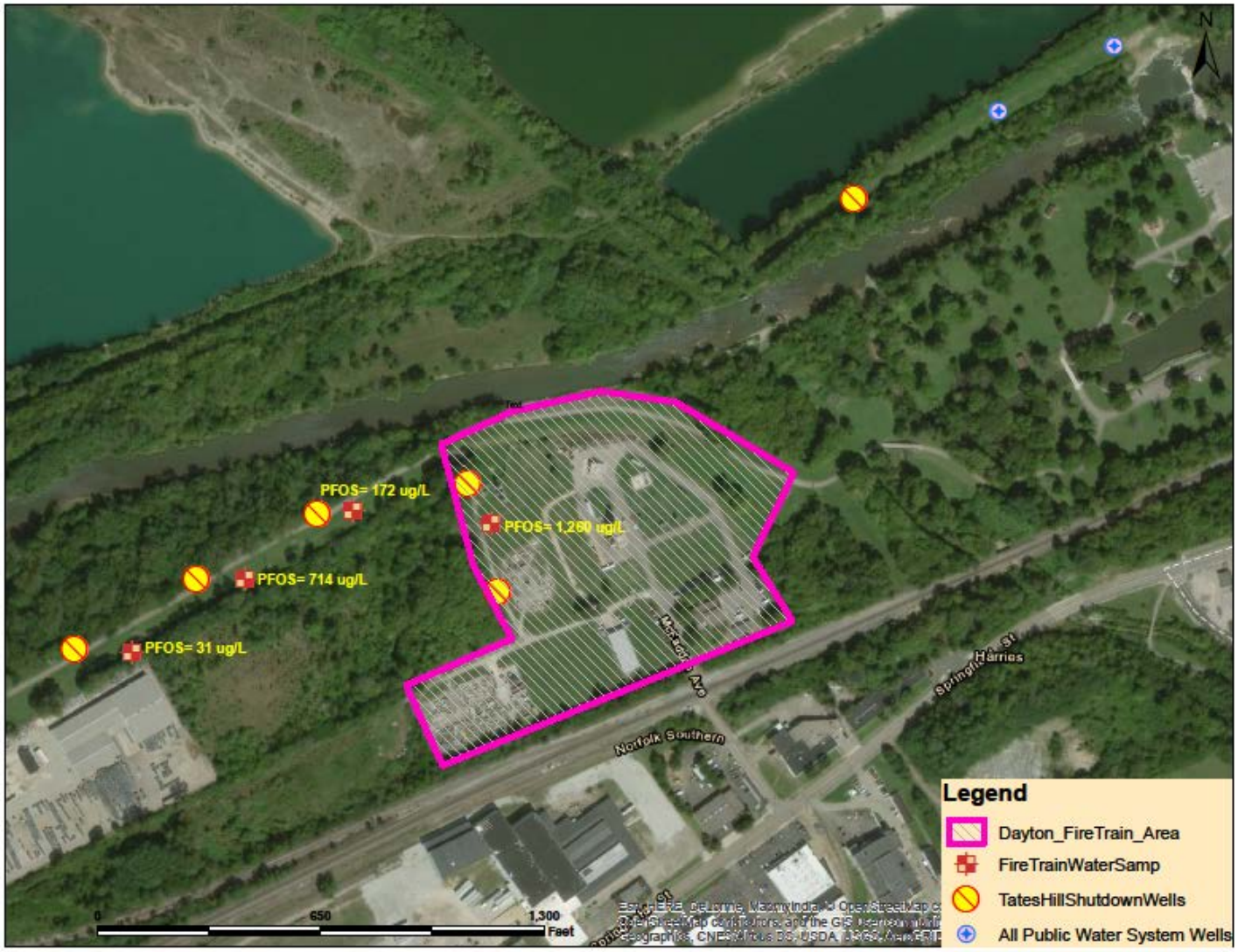
Dayton Fire Training Area



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Ohio EPA Instructions to Dayton

Mitigate ongoing releases at the Fire Training Center

Characterize and address threats to the Mad River Wellfield

Determine if the Fire Training Center is the source of low-level, raw water PFAS detection at the Ottawa Treatment Plant

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Ohio EPA Proactive Drinking Water Sampling

Priority: Investigate whether there could be additional areas where drinking water is contaminated with PFAS

Reasons: Wide use, persistence, low HAL, not widely tested
New contamination continues to be found
Ohio's industrial heritage

Approach: Sampling of wells near potential PFAS sources

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Evaluation of Sampling Techniques

Challenge: Minimizing cross-contamination when chemicals are widespread and measuring at ppt level

1 ppt = 1 in^2 in 250 mi^2

1 sec in 32,000 years

1 ounce in 7.5 billion gals

Approach: Follow normal sampling procedures, but with special precautions

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Sampling Considerations: Personal Hygiene

- Avoid cosmetics, moisturizers, hand creams, etc.
- Avoid surfactants like shampoos, conditioners, and body gels immediately prior to sampling
- Bar soap (without moisturizing lotions) is acceptable
- Avoid sunblock and insect repellants that contain PFAS
- Wash hands frequently during sampling

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Sampling Considerations: Field Equipment

- No Teflon or low density polyethylene (LDPE)
- No waterproof field books
- No markers, except for Sharpies
- No post-it notes

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Sampling Considerations: Gear/Clothing

- No Gore-Tex™ or Tyvek®
- No synthetics, stain resistance, or water-proofing
- Cotton laundered without fabric softeners and dryer sheets is preferred
- New clothing should be washed at least six times after purchase
- Disposable, powderless nitrile gloves should be worn and changed often

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Additional Sampling Considerations

- Any stain-resistant field vehicle seats should be covered with a well-laundered blanket or sheet

- Field QA/QC is highly important
  - Field blanks
  - Field duplicates

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Determining Whether and Where to Sample

Can pathways to off-site drinking water wells be reasonably anticipated?

Consider:

- Verify PFAS presence
- Where used or managed
- Ground water flow direction
- Location of drinking water wells

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Involving Local Health Departments

Most sampling will likely be at private wells

Pre-Sampling Meetings

- OEPA / ODH / Local Health District
- Finalize sampling plans
- Discuss challenges of sampling for PFAS
- Discuss roles

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Sampling Process

- Knock on doors rather than schedule in advance
- If residents are not home:
  - Leave fact sheet
  - Contact information
- If residents are home:
  - Explain purpose and ask to sample an outdoor faucet
  - If approved, collect basic information
- Send samples to lab
- Send results to owner with a copy to local health
- Assistance from local health on exceedances

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Ohio EPA Sampling Near Air Bases

September 2016 – April 2017

Reasons for initial focus on air bases:

- Fire training activities are high risk for contaminating ground water
- Ohio Air National Guard is a fellow state agency
- Federal PFAS size investigations would not occur for another 1-2 years
- Need for proactively sample wells at risk

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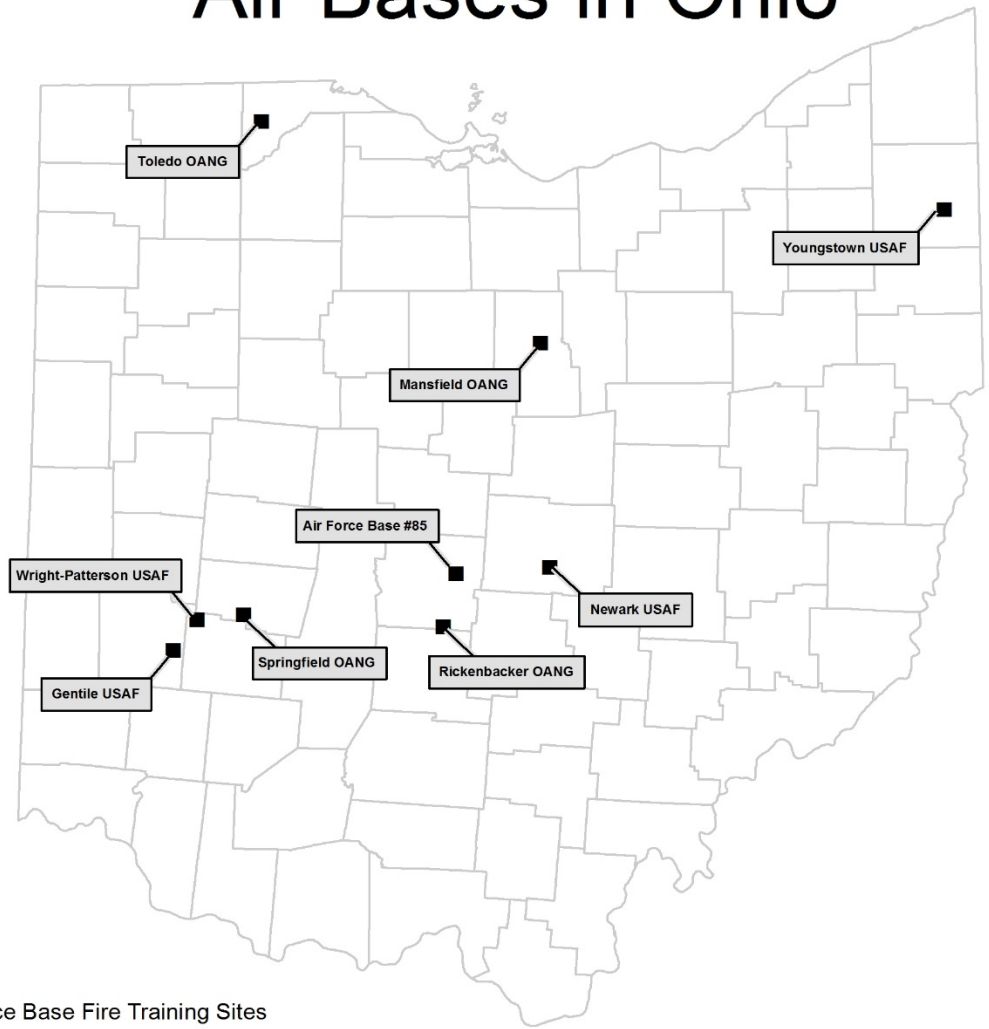
Ohio Air Bases

Air Bases in Ohio



Legend

- Ohio DoD Air Force Base Fire Training Sites

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March 16, 2018

Youngstown-Warren U.S. Air Force Base

- Assisted by Trumbull County Health Department
- Relatively few wells in area
- Four wells sampled in several directions
- All ND for PFOS and PFOA

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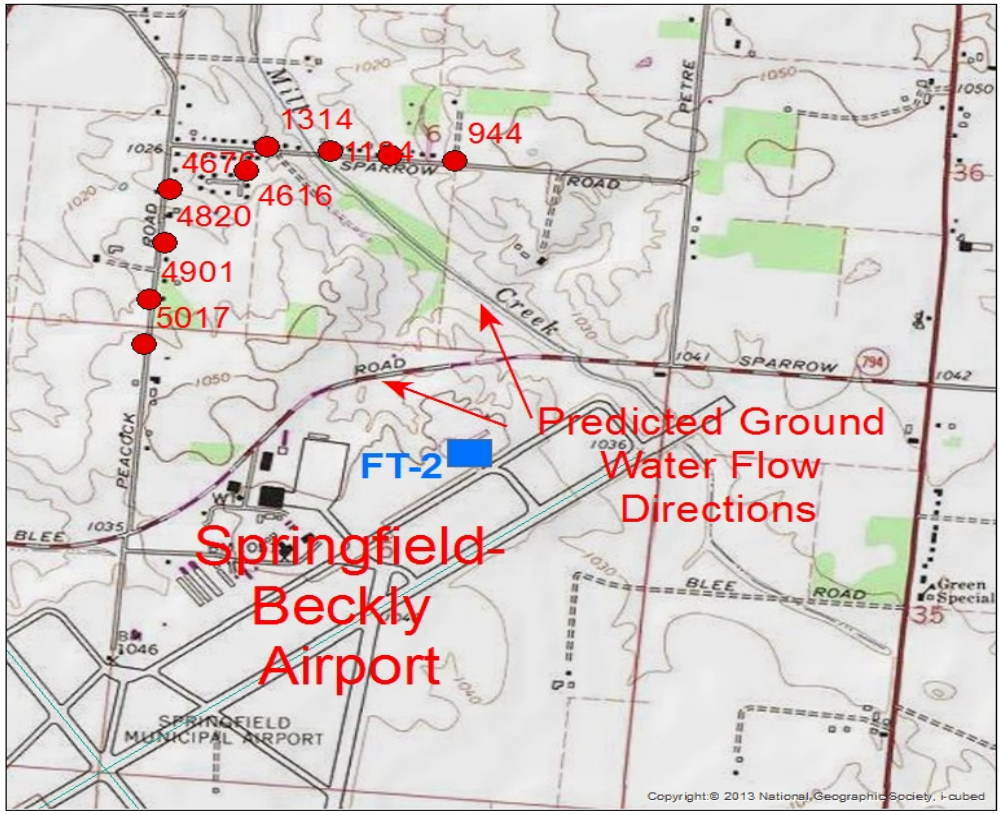
Springfield OANG Base

- Assisted by Clark County Combined Health District
- Many wells in area
- Nine wells sampled
- All were ND for PFOS and PFOA



Domestic Wells Targeted for Ground Water Sampling Springfield ANG

Home Numbers along Peacock Road (N-S) and Sparrow Road (E-W) in Red

N

0 0.075 0.15 0.3 Miles

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Mansfield OANG Base

- Assisted by Richland County Health Department
- Focused on Mansfield-LAHM Airport
- Sampled three wells
- All samples were ND for PFOS and PFOA

Richland Shale Road Area Mansfield-Lahm Airport

PFC Sampling Summary Dec. 20, 2016 and Jan. 3, 2017

0 0.05 0.1 0.2 Miles

N

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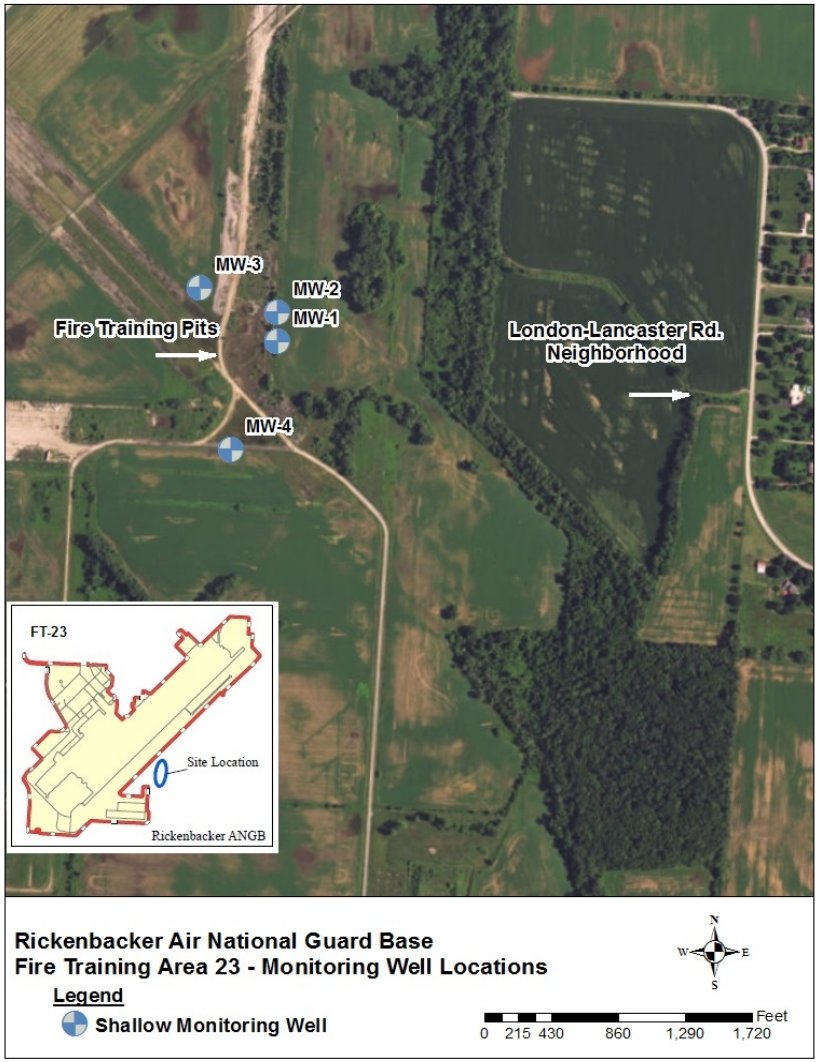
Rickenbacker



- Former fire training area is on land currently owned by Columbus Regional Air Authority
- Private wells to the east in presumed direction of ground water flow, but not sampled
- Samples collected from four on-site monitoring wells installed by CRAA between FTA and private wells installed by CRAA
- All samples were ND for PFOS and PFOA

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Toledo Air National Guard Base

- Assisted by Toledo-Lucas County Health Department
- Sampled 16 private wells
- All samples were ND for PFOS
- PFOA was detected in 7 wells:
  - One was >70 ppt (349 ppt)
  - Three were between LOQ and HAL, including one at 59 ppt
  - Three wells had detections below the LOQ

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Toledo – Response to HAL Exceedance

Immediately upon receiving lab results, OANG/Toledo-Lucas Co Health Dept. visited residents at home with 349 ppt PFOA and offered bottled water

Offer was accepted, and OANG has provided bottled water and now is arranging for the home to be connected to a public water system

Residents at homes with 59 ppt declined bottled water

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Future PFAS Sampling

There are many potential sources besides fire training at air bases

Have benchmarked with other states on identifying the probable industry sectors , and worked with other agencies/divisions to locate them in Ohio

Will decide where to sample based on the source and how likely it is to contaminate, as well as the environmental sensitivity

Plan to follow the same process and involve local health departments when private wells are sampled

Sampling to possibly begin May

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Questions?

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