


2020 NACAA Joint Permitting and Enforcement Workshop
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# PFAS EMISSIONS INVESTIGATION

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PER- AND POLYFLUOROALKYL SUBSTANCES

# INTRODUCTION TO PFAS

A large, complex, and ever-expanding group of man-made chemicals.

PFAS molecules are made up of a chain of linked carbon and fluorine atoms.

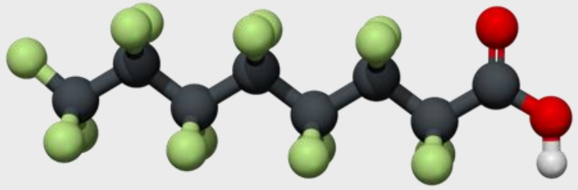
PFAS do not degrade in the environment.

Historically, research has focused on two kinds of PFAS:

- Perfluorooctanoic Acid (PFOA)
- Perfluorooctane Sulfonate (PFOS)

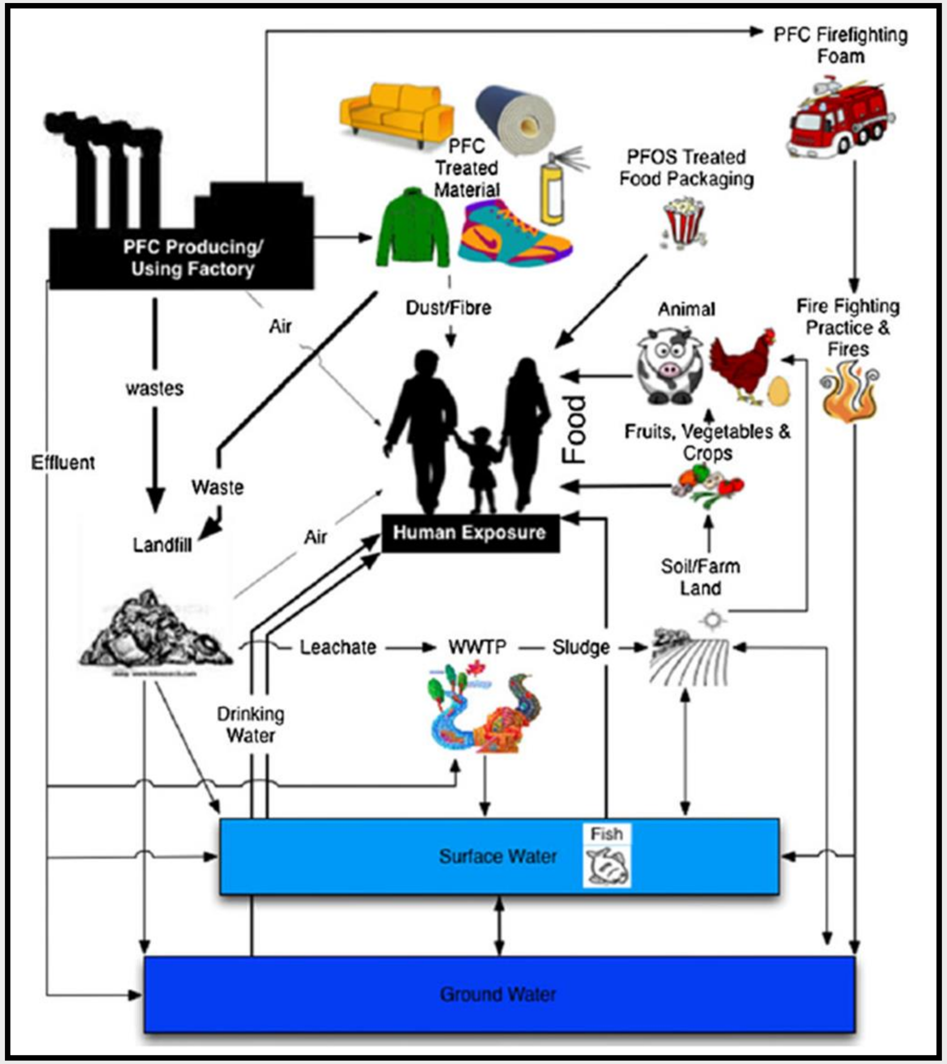
These two compounds are no longer made in the U.S. but chemical manufactures have replaced them with alternative PFAS such as:

- GenX
- ADONA



Example of molecular structure of Perfluorooctanoic Acid (PFOA)

# POSSIBLE SOURCES OF PFAS RELEASES




From Oliaei 2013, Environmental Science Pollution Research

Used for decades to make products that resist heat, oils, grease, stains and water

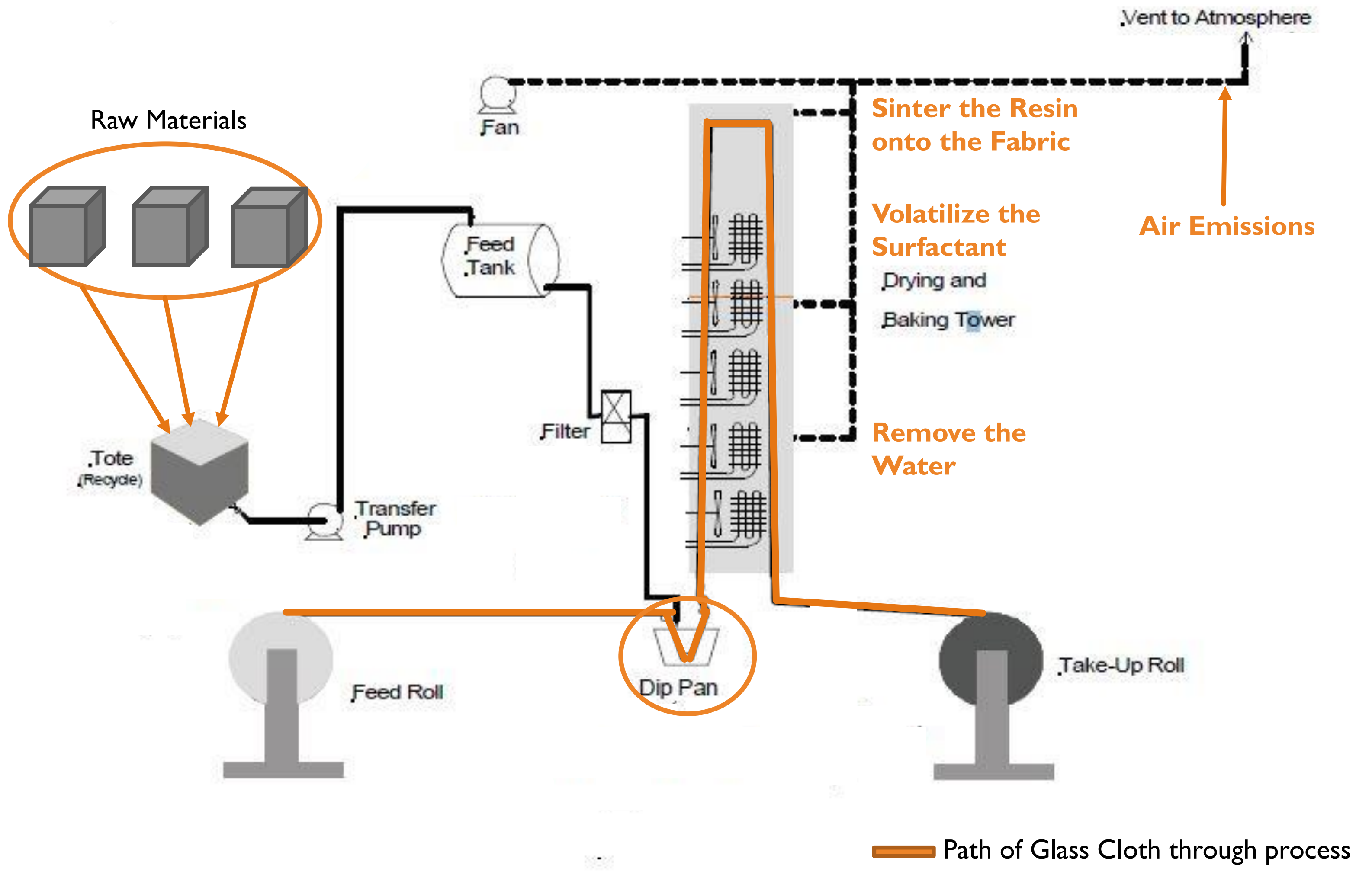
- Textiles, Upholstery, Apparel and Carpets
- Paper, Packaging, Non Woven Fibers
- Metal Plating (mist suppressant)
- Semiconductors
- Wire Coating
- Medical Tubing
- Firefighting Aqueous Film-Forming Foam

New Hampshire Department of Environmental Services

# FACILITY OVERVIEW

# FABRIC COATERS

## TYPICAL GLASS CLOTH PROCESS DIAGRAM



Facility-wide Permit Limit 50 tpy VOCs

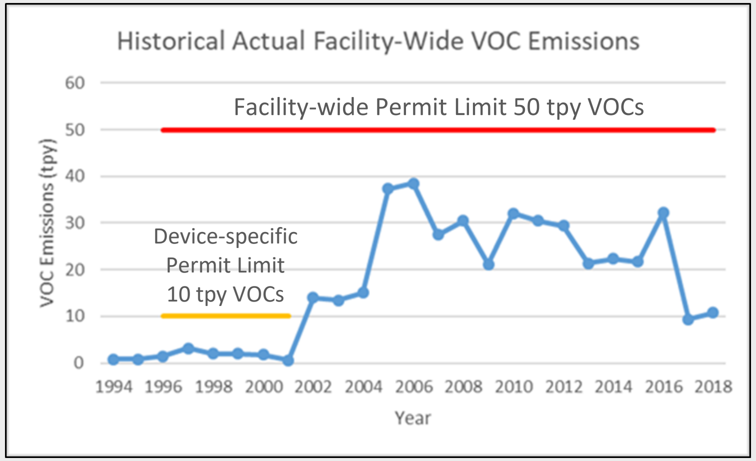
# REGULATORY REQUIREMENTS

# FACILITY-WIDE LIMITATIONS

NH State Statute RSA 125-C, *Air Pollution Control*
Env-A 600, *Statewide Permit System*

# FACILITY-WIDE EMISSION LIMITATIONS

## Volatile Organic Compounds (VOCs) < 50 tpy




## Hazardous Air Pollutants (HAPs) < 10 tpy each & 25 tpy combined

| HAP | Highest Actual Emissions* (2012 – 2018) | HAP Limitation in Permit |
|---|---|---|
| Ethylene Glycol | 4.1 tpy | 10 tpy |
| Toluene | 3.6 tpy | 10 tpy |
| Hydrogen Fluoride* | 1.1 tpy | 10 tpy |
| Miscellaneous HAPs | 0.2 tpy | 10 tpy each |
| TOTAL | 9.0 tpy | 25 tpy |

* Based on future projected emissions after installation and operation of regenerative thermal oxidizer

REGULATORY REQUIREMENTS

NH AIR TOXICS REGULATION

NH State Statute RSA 125-C, *Air Pollution Control*
NH State Statute RSA 125-I, *Air Toxic Control Act*
Env-A 1400, *Regulated Toxic Air Pollutants*

# NH AIR TOXICS REGULATION (Inhalation-based Standards)

- NH State Statute: RSA 125-I, *Air Toxic Control Act*
  - Defines Regulated Toxic Air Pollutant (RTAP)
  - Outlines methodology for adoption of ambient air limits (AALs)
  - Authorizes NH Air Regulation: Env-A 1400, *Regulated Toxic Air Pollutants*
- Env-A 1400, *Regulated Toxic Air Pollutants*
  - Contains the list of RTAPs and AALs
  - Ammonium perfluorooctanoate (APFO) is a listed RTAP with established AALs
  - APFO + $H_2O$ —disassociates→ PFOA
- 2006 Administrative Order required reduction of APFO in raw materials thereby reducing PFOA emissions from the facility in order to protect against inhalation health risks (AALs).

# APFO CONCENTRATIONS & DETECTION LEVELS IN RAW MATERIALS

**2005**
2,000 ppm
Prior to reformulation by suppliers (EPA Stewardship Agreement) and NHDES Administrative Order

**96+% reduction**

**2007**
75 ppm
After 2006 NHDES Administrative Order

**99+% reduction**

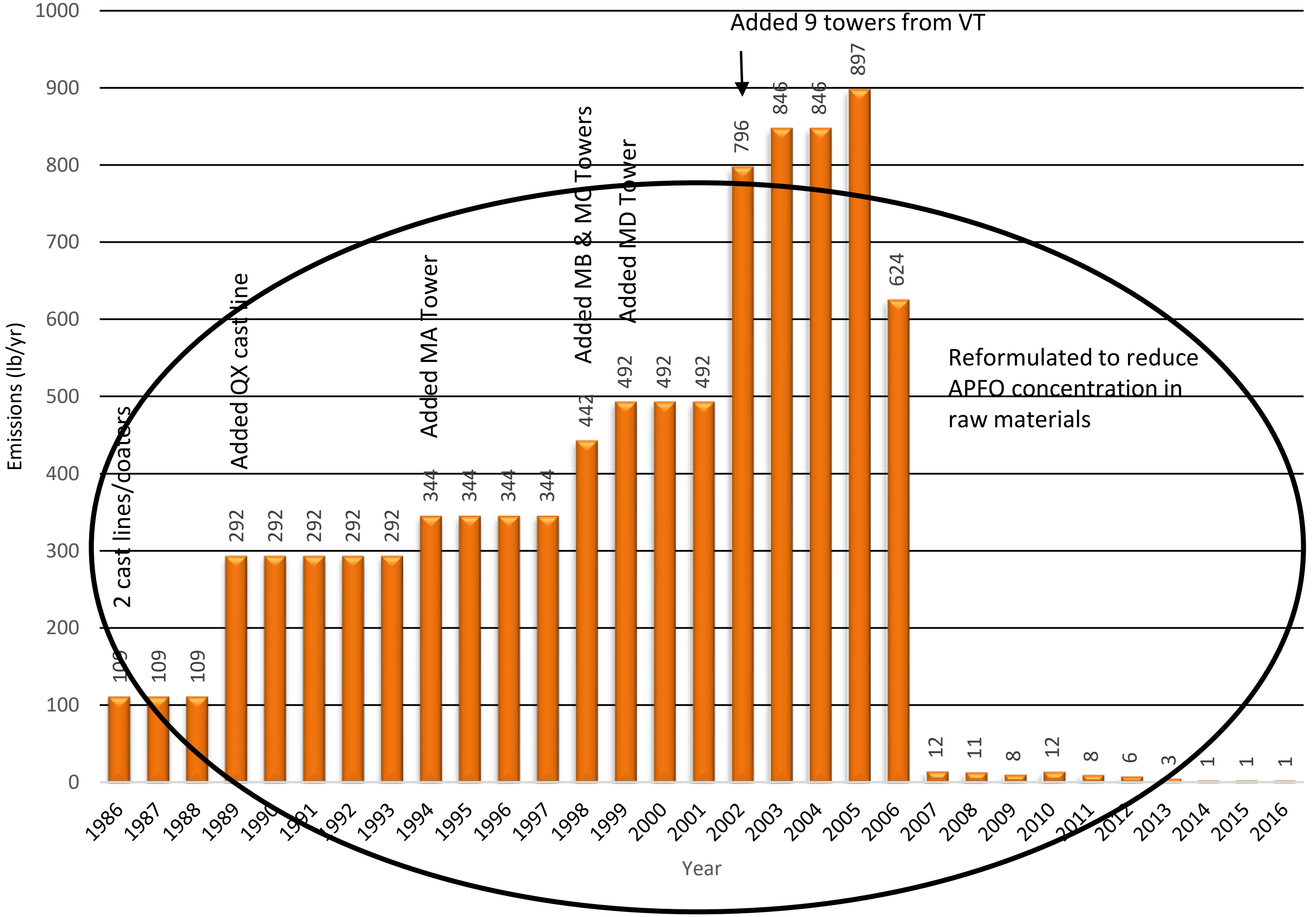
**2016**
< 0.13 ppm
APFO concentration reported as non-detect. Detection level for 2016 analysis

**2016**
< 0.05 ppm
APFO concentration reported as non-detect. Detection level for 2016 analysis

**2018**
< 0.0025 ppm
Detection level for 2018 analysis

**2018**
0.021 - 0.025 ppm
APFO concentration reported


# ESTIMATED HISTORICAL PFOA AIR EMISSIONS




**Total PFAO Emissions over 30 years:**
**4.6 tons**

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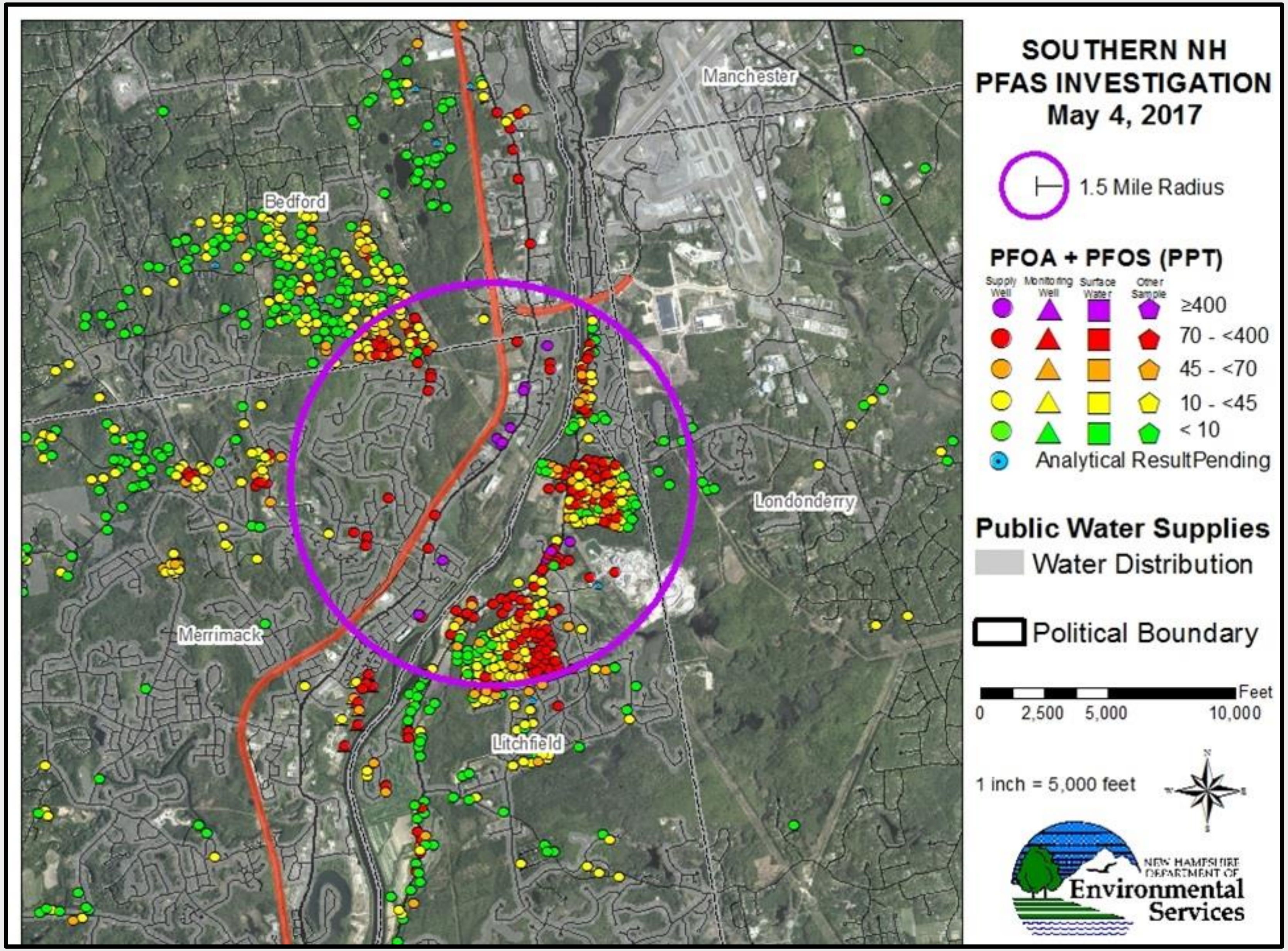
# SOUTHERN NH PFAS INVESTIGATION



# AIR DEPOSITION MODELING

- To identify where additional private well sampling should be done
- To determine the size/shape of deposition area
- Identification places to further evaluate during the site investigation (e.g. soil or groundwater testing)

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Dip Pan Sampling

Stack Residue/Char

Stack Emission Sampling

Roof Top Wipes Sampling

Dust

# NH STATE STATUTE RSA 125-C:10-e

## *Requirements for Air Emissions of Perfluorinated Compounds Impacting Soil and Water* (BACT Law) – September 2018

## September 2018: NHDES letter to Facility

- PFOA, PFOS and other PFAS compounds were found in raw materials, stack emissions, stack residue/char, roof top, and dust.
- NHDES letter notified the facility that they were subject to the BACT Law and required the submittal of a permit application and BACT analysis within 6 months.

## March 2019: Facility submitted application and BACT analysis for installation of RTO

Pilot Scale Fiberbed Mist Collection System

# PFAS REGULATION AND CONTROL EQUIPMENT

# BACT LAW

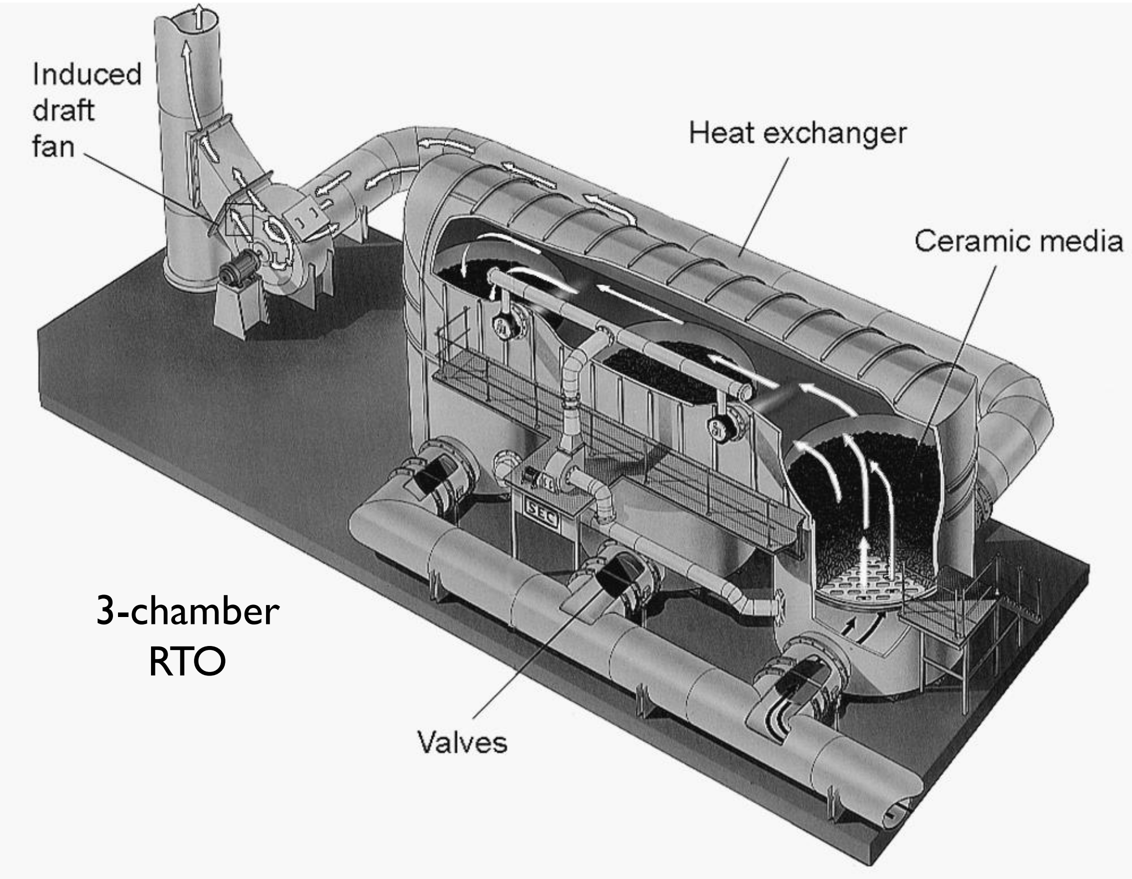
NH State Statute RSA 125-C:10-e, *Requirements for Air Emissions of Perfluorinated Compounds Impacting Soil and Water*

## CONTROL TECHNOLOGY OPTIONS

| Regenerative Thermal Oxidizer (RTO) | Recuperative Thermal Oxidizer | Catalytic Oxidation | Filtration Systems (Fiberbed Mist Collection System) | Absorption (Scrubber) |
|---|---|---|---|---|
| Highest control effectiveness | Similar control effectiveness of RTO | Lower control effectiveness than oxidizers | Limited efficiency when piloted in 2018 | Low control effectiveness |
| Best thermal efficiency | Lower thermal efficiency than RTO | Susceptible to catalysts poisoning, blinding and fouling | Questionable effectiveness for all PFAS | Transfers PFAS from gas to liquid stream; water treatment and disposal issues |
| Ability to reduce all PFAS regardless of carbon chain length | Increased fuel usage = Increased air pollution | Not appropriate for particles and moisture | High electrical and energy demand; water treatment and disposal issues | |

Most ← → Least

**INCREASING CONTROL EFFECTIVENESS**




Source: US EPA APTI 415: Control of Gaseous Emissions

## WHAT IS THERMAL OXIDATION?

- Use combustion to convert pollutants ⟶ $CO_2$ + $H_2O$
- Combustion of PFAS will result in hydrogen fluoride (HF) emissions as well.

## GOAL OF THERMAL OXIDATION FOR PFAS

- Break the C-F bonds with complete combustion no matter carbon chain length.

## BENEFIT OF 3- vs. 2-CHAMBER DESIGN

- During chamber switching, a brief transition period occurs where a small volume of untreated air may bypass the treatment and vent directly to the atmosphere.
- A 3-chamber design serves to receive that small volume of untreated air and reintroduce it to the treatment bed during the subsequent cycle.

# FINAL PERMIT REQUIRED WORK PRACTICE STANDARDS FOR RTO

EPA

www.epa.gov/research

## Technical BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

### Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams

**Background**

Per- and polyfluoroalkyl substances (PFAS) are a very large class of man-made chemicals that include PFOA, PFOS and GenX chemicals. Since the 1940s, PFAS have been manufactured and used in a variety of industries in the United States and around the globe. PFAS are found in everyday items such as food packaging, non-stick stain repellent, and waterproof products, including clothes and other products used by outdoor enthusiasts. PFAS are also widely used in industrial applications and for firefighting. PFAS can enter the environment through production or waste streams and can be very persistent in the environment and the human body. PFAS have many and varied pathways into waste streams, presenting challenges for ultimate disposal. Determining the appropriate method for ultimate disposal of PFAS wastes is a complex issue due to their volatility, solubility, and environmental mobility and persistence. EPA is currently considering multiple disposal techniques, including incineration, to effectively treat and dispose of PFAS waste.

**Options and Considerations for the Disposal of PFAS Waste via Incineration**

One potential disposal method for PFAS waste is through high temperature chemical breakdown, or incineration. Incineration has been used as a method of destroying related halogenated organic chemicals such as polychlorinated biphenyls (PCBs) and ozone-depleting substances (ODSs), where sufficiently high temperatures and long residence times break the carbon-halogen bond, after which the halogen can be scrubbed from the flue gas, typically as an alkali-halogen. PFAS compounds are difficult to break down due to fluorine's electronegativity and the chemical stability of fluorinated compounds. Incomplete destruction of PFAS compounds can result in the formation of smaller PFAS products, or products of incomplete combustion (PICs), which may not have been researched and thus could be a potential chemical of concern.

Incineration of halogenated organic compounds occurs via unimolecular decomposition and radical reaction. For unimolecular decomposition, fluorinated organic compounds require temperatures above 1,000°C to achieve 99.99% destruction in 1 second residence time. Unimolecular decomposition of highly fluorinated organics most likely occurs through breakage of C-C or C-F bonds (Tsang et al., 1998). The most difficult fluorinated organic compound to decompose is $CF_4$, requiring temperatures over 1,400°C, but is easily monitored, making it a potential candidate for destructibility trials.

Fluorinated organic compounds can also be degraded via incineration by free radical initiation, propagation, and branching mechanisms. Although hydroxyl radical reaction with hydrocarbons is a common combustion flame-propagating mechanism, the strength of the C-F bond makes this pathway unlikely and would instead leave atomic hydrogen, formed at high temperatures, as the likely radical reacting with the carbon-bonded fluorine.

1 U.S. Environmental Protection August 2019

| | |
|---|---|
| Temperature | Minimum temperature of 1000°C (1832°F) |
| Time and Turbulence | Minimum gas residence time of 1 second with flow rate not to exceed 70,000 scfm |
| Destroys PFAS regardless of carbon chain length | Oxidizes PFAS whether an Ambient Groundwater Quality Standard (AGQS) or Surface Water Quality Standard (SWQS) exists or not |


# STACK TESTING

2005 – 2016 – 2018

Modified Method 5
3 Impingers
XAD Traps – Front and Back-half Filters
SUMMA Canisters

EPA ORD Methods Development

OTM-45 and Destruction Method - 2020

# SCHEDULE OF NEXT SIGNIFICANT MILESTONES

**NHDES ARD DIRECTOR'S DECISION and FINDINGS OF FACT**

February 11, 2020

Appeal Deadline March 12, 2020

**FACILITY SUBMITTING MONTHLY PROGRESS REPORTS**

**COMPLETE CONSTRUCTION AND INSTALLATION OF RTO**

Within 12 months of permit issuance

**CONDUCT INITIAL STACK TESTING**

Within 60 days of startup of the RTO

# QUESTIONS

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