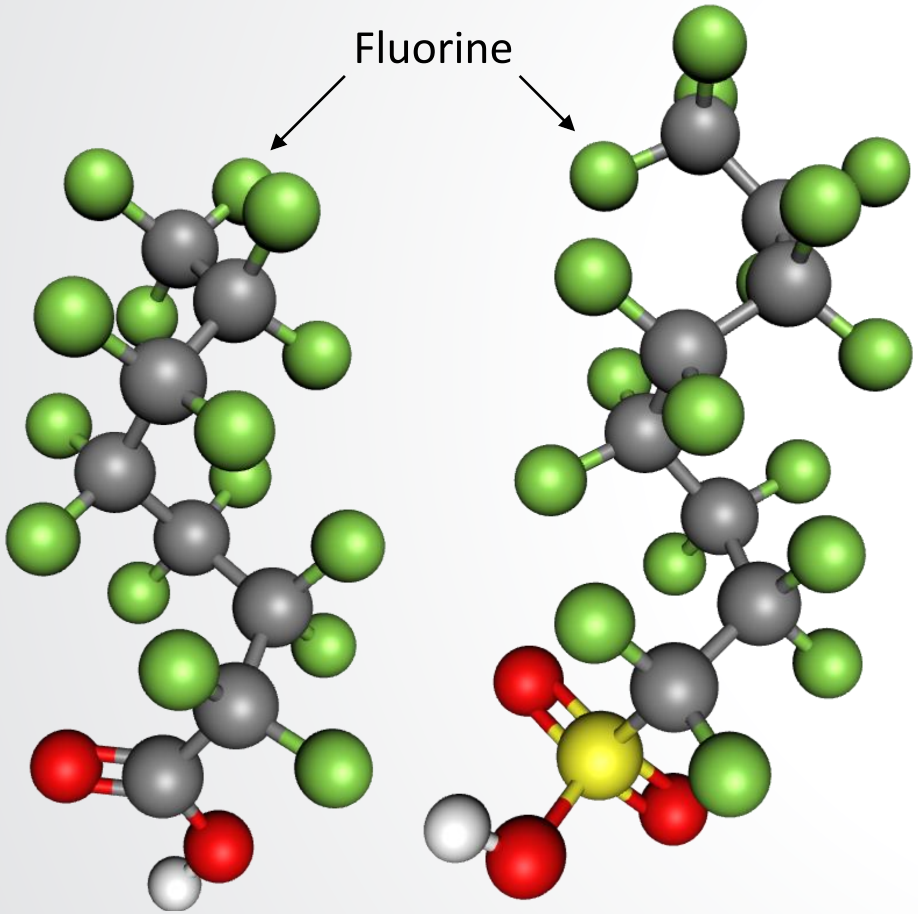
PFAS Fate and Remediation: Treatment Methods and Residual Waste Streams

Phillip Potter, USEPA Center for Environmental Solutions and Emergency Response

Per- and Polyfluoroalkyl Substances (PFAS)



Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)

A large class of synthetic chemicals

- Features chains of carbon atoms surrounded by fluorine atoms
- Wide variety of chemical structures, from single molecules to polymers

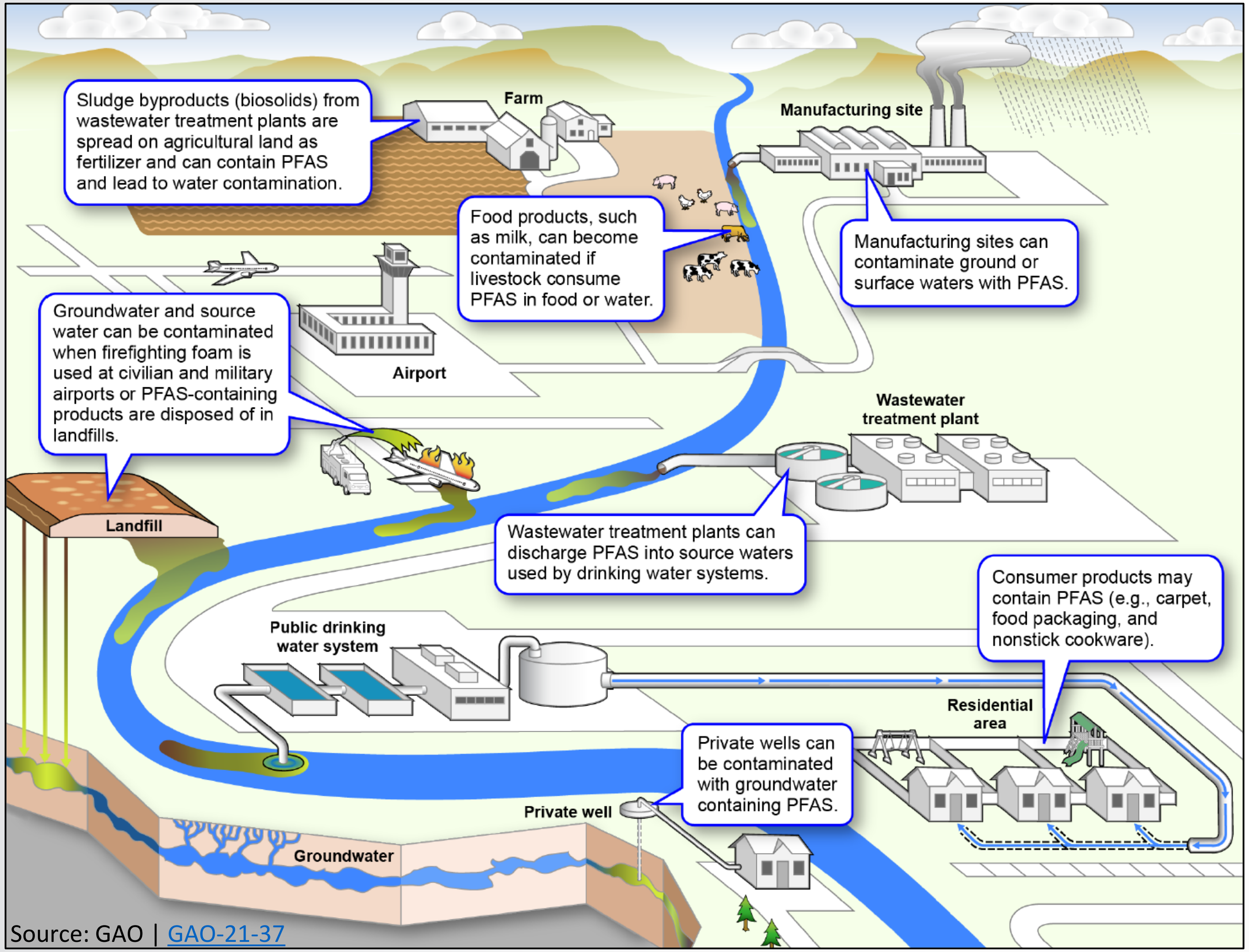
Used in homes, businesses and industry since the 1940s

- Have been detected in soil, water and air samples
- Most people have been exposed to PFAS

Some PFAS are known to be PBT

- P = Persistent in environment and through treatment
- B = Bioaccumulative in organisms
- T = Toxic at relatively low levels (ppt)

Sources of PFAS in the Environment



Source: GAO | GAO-21-37

- Direct release into the environment
  - Use of aqueous film-forming foam (AFFF) in training and emergency response
  - Release from industrial facility
- Landfills and leachates from PFAS-containing products
- Wastewater treatment discharge and biosolids
- PFAS are found in air, soils, plants, biota, water, and sediments
- This presentation will cover drinking water treatment, including the management of residuals

Destruction & Disposal

Data Gap: Knowledge regarding end-of-life management and ultimate disposal of PFAS-containing materials

Actions:

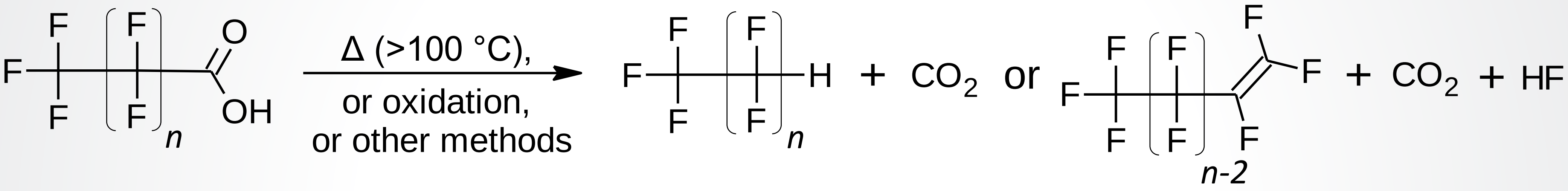
- Characterize end-of-life PFAS disposal streams (e.g., municipal, industrial, manufacturing, recycled waste streams)
- Evaluate efficacy of disposal/destruction technologies (e.g., landfilling, incineration, *in situ* stabilization) to manage end-of-life disposal
- Evaluate possibility of products of incomplete combustion/destruction

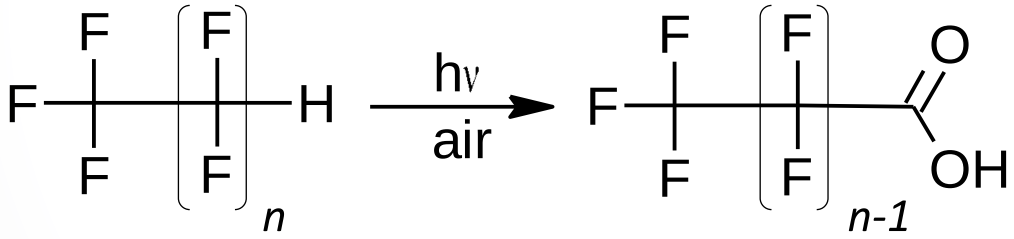
Research Products:

- PFAS presence in different types of landfills and leachates
- PFAS behavior in incineration environments
- Thermal treatment of PFAS-contaminated biosolids

Impact: Responsible officials will be able to effectively manage end-of-life disposal of PFAS-containing materials

Easily transformed, but not destroyed





- Parent molecule is easily transformed to a more volatile PFAS
- Products of Incomplete Combustion (PICs)
- Only looking at destruction efficiency is misleading
- Air emissions sampling and analyses are critical to understanding the fate of PFAS in a treatment method

LaZerte, J. D.; et al. *JACS,* **1953,** *75* (18), 4525-4528.
Ellis, D. A.; et al. *Nature* **2001,** *412* (6844), 321-324.

Method development

Which PFAS are in the environment?

How much PFAS is present?

Targeted vs. Non-Targeted Methods

- **Targeted methods** measure a specific, defined set of known analytes
  - Analytical standards exist for quantitation
  - Method “sees” analytes on the targeted list and will not “see” other analytes
  - Once the analysis is complete, cannot go back for other analytes
- **Non-targeted methods** use high-resolution mass spectrometry to identify all analytes in the sample (known and unknown)
  - Limited ability to quantify analytes
  - Used to screen for lists of known suspects or discover unknown analytes
  - Can use stored data to look for analytes that were unidentified at the time of analysis
- **“Total PFAS” methods** isolate and measure organic fluorine
  - Potential use in screening samples for PFAS (faster than non-targeted methods)
  - Requires more development to lower detection limits and understand limitations

Environmental Measurement

Reliable analytical methods are needed to identify and measure PFAS in air, water and land

Recent Accomplishments

Air

- OTM-45 (air emissions; 2021)

Water

- EPA Method 533 (drinking water; 2019)
- EPA Method 537.1 (drinking water; 2018/2020)
- SW-846: Method 8327 (wastewater, groundwater, surface water; 2021)
- Draft Method 1633 (water, solids, tissue; 2021)
- Draft Method 1621 (wastewater; 2022)

Current & Ongoing Efforts

Air

- Develop and test methods for additional PFAS in air emissions
- Whole air sampling – canister (OTM)

Land / Water / Tissues

- Support multi-laboratory validation of Draft Method 1633 and Draft Method 1621

Other Methods

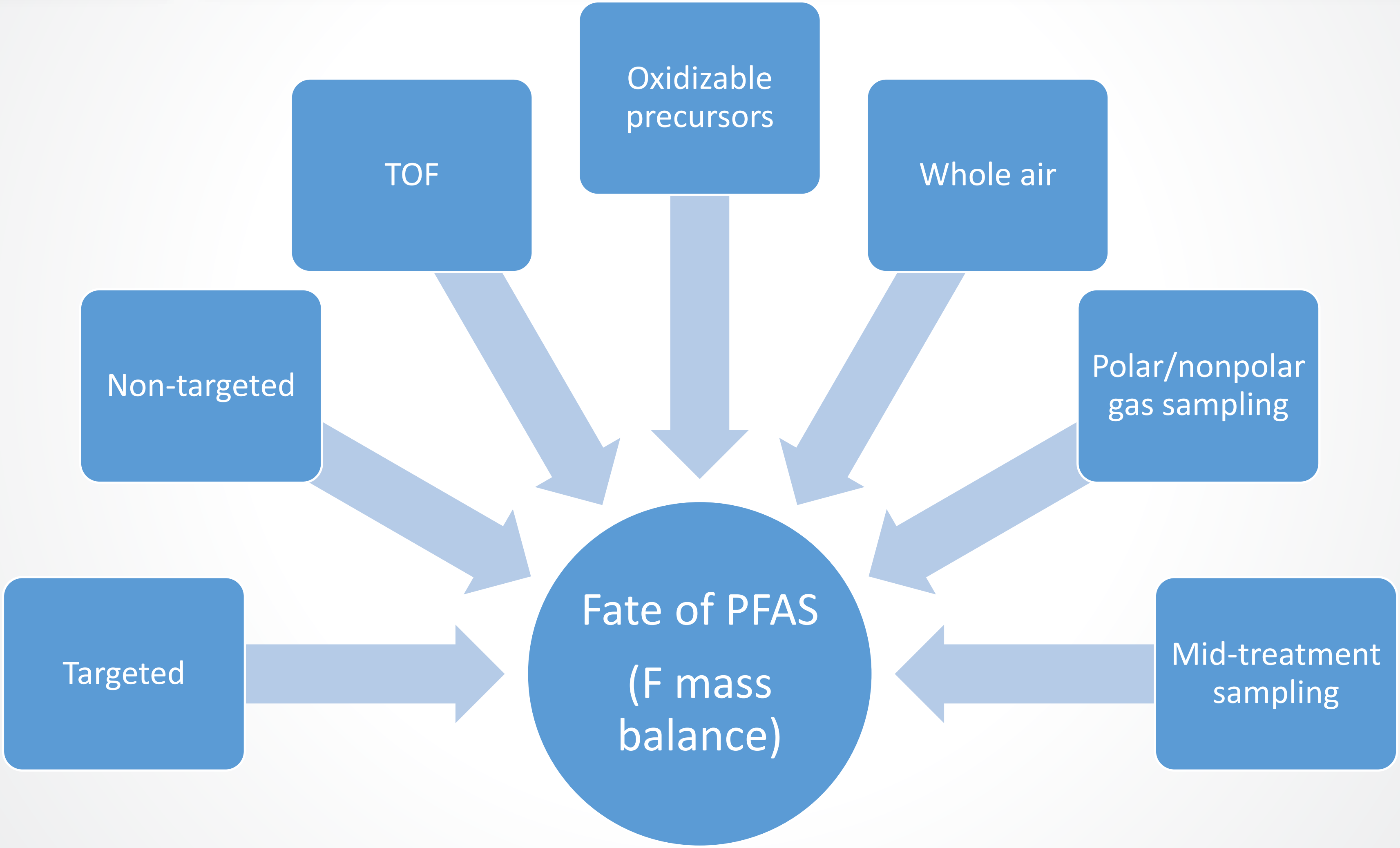
- Develop "total PFAS" methods
- Refine non-targeted analysis methods

Future ORD PFAS Analytical Work

Potential Work:

- Develop additional targeted methods for priority PFAS in environmental matrices
- To evaluate lower detection levels for the AOF/CIC method and test AOF/CIC technique for other matrices
- To evaluate other approaches that may capture more PFAS while not capturing inorganic fluoride or fluoride associated with other organic molecules (e.g., pesticides)
- Continuing work with Total Organic Precursors (TOP) to identify total PFAS load which may degrade to most persistent PFAS
- Developing and testing ambient air and emissions sampling and analysis methods
- Continued development and application of nontargeted (HRMS) methods for discovery of novel PFAS, suspect screening analysis, and identification of transformation products.

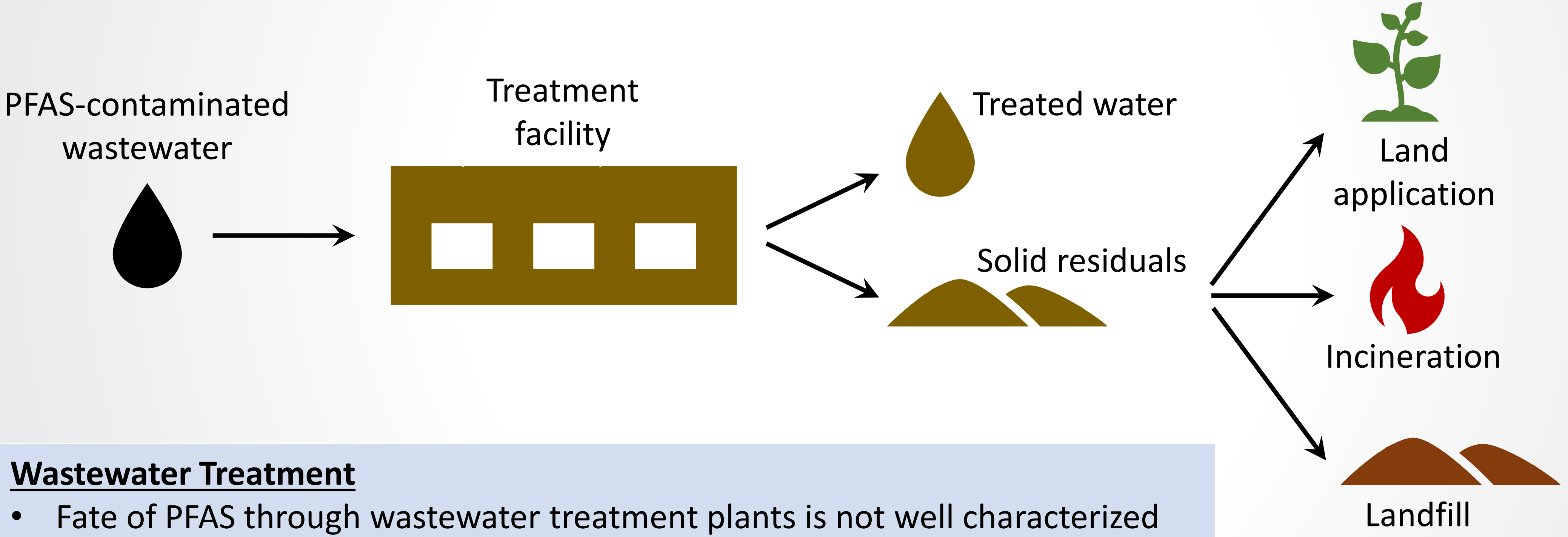
Everything but the kitchen sink



Wastewater

Wastewater Treatment

How do we remove PFAS from wastewater?



<u>Wastewater Treatment</u>

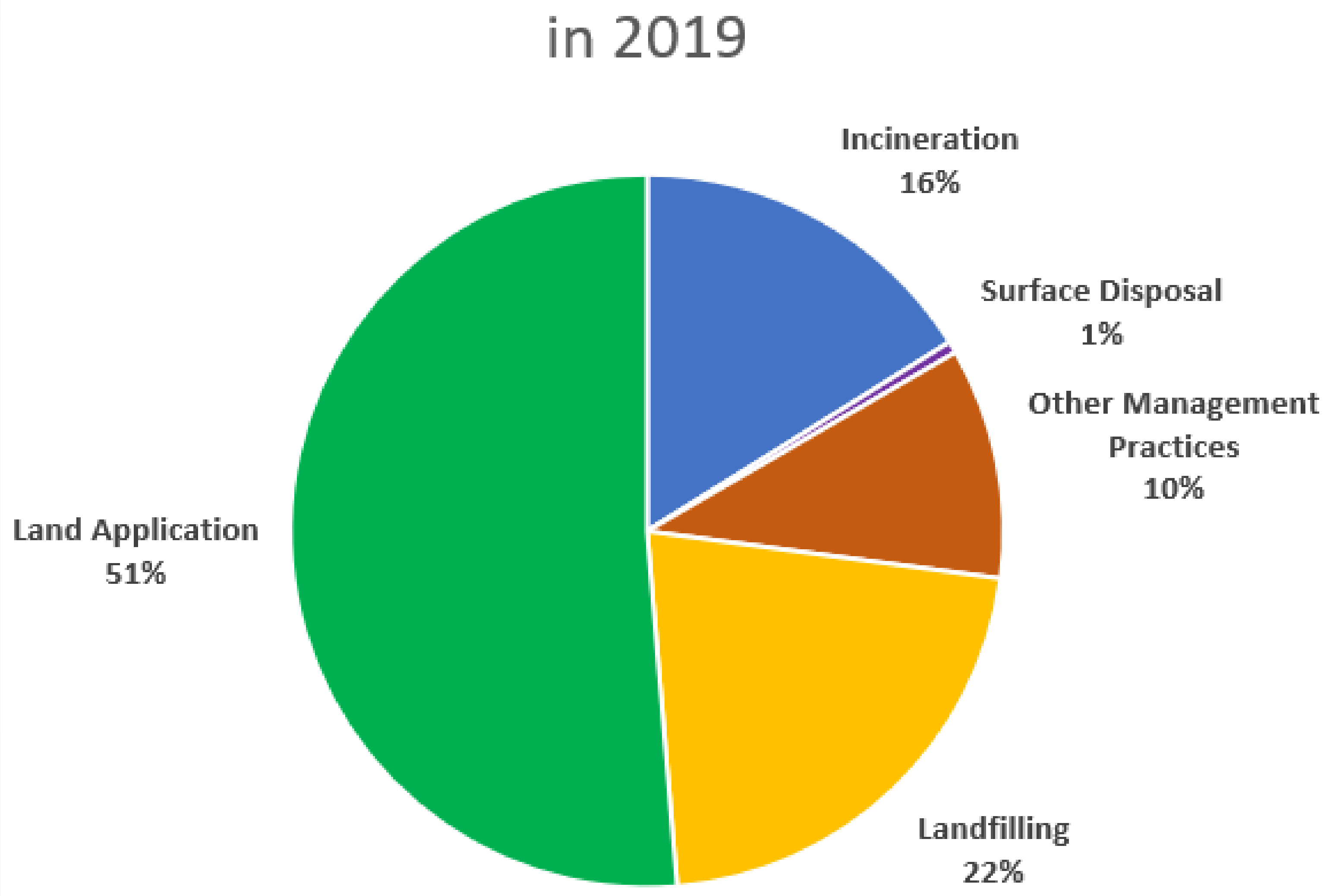
- Fate of PFAS through wastewater treatment plants is not well characterized
- PFAS are found in solid residuals and, subsequently, biosolids
- Some management approaches for solid residuals can release PFAS into the environment
- Pretreatment practices are likely more effective that central treatment

Temporal and Spatial Wastewater Sampling

Project to…

- Gain a better understanding of the temporal variability of PFAS concentrations entering wastewater facilities
- To evaluate the fate of PFAS through wastewater treatment
- To determine the concentrations of PFAS in residual streams over time with an eye toward studying disposal options

Biosolids Use & Disposal



2019 EPA electronic reporting data available [Enforcement and Compliance History Online (ECHO)]

State Responses

Example: The State of Maine has taken action on biosolids applications

Per- and Polyfluoroalkyl Substances (PFAS)

Updates

Managing PFAS in Maine, Final Report from the Maine PFAS Task Force, January 2020

February 2020 Maine PFAS Mapper (Under Development), please direct any feedback to pfas.dep@maine.gov

September 6, 2019 - Maine sludge and bioash spreading information (Excel), please note the file contains links that will not work. Please direct any feedback to pfas.dep@maine.gov

Maine PFAS data (2007-2020) as of June 2, 2020. For questions regarding this data, please email pfas.dep@maine.gov

August 14, 2019 Emergency Sludge Dewatering State Wastewater Infrastructure Planning and Construction Grants Available

June 10, 2019 letters from the Northeast Committee on the Environment to US Committee on Environment and Public Works and Congressional PFAS Task Force.

On March 22, 2019, the Department notified sludge/biosolids program licensees and related composting facilities of a new requirement to test for PFOA, PFOS, and PFBS. Upcoming deadlines include submission of an updated Sampling and Analytical Work Plan by April 12, 2019, and initial sampling to be conducted by May 7, 2019.

- March 22, 2019 memo re: Requirement to analyze for PFAS compounds. Includes sampling protocol and list of approved laboratories for PFAS analysis. (pdf)
- Per- and Polyfluoroalkyl Substances (PFAS) Laboratory Recommendations follow-up memo (pdf)

DEP Announces Testing of All Sludge Materials Before Land Application

Governor Mills Signs Executive Order Establishing Task Force Charged with Studying Effects of PFAS Prevalence in Maine

https://www1.maine.gov/dep/spills/topics/pfas/index.html

Follow the Leader? Maine's Strict Stance on PFAS and Biosolids Land Application Sets the Stage for Further State Regulation

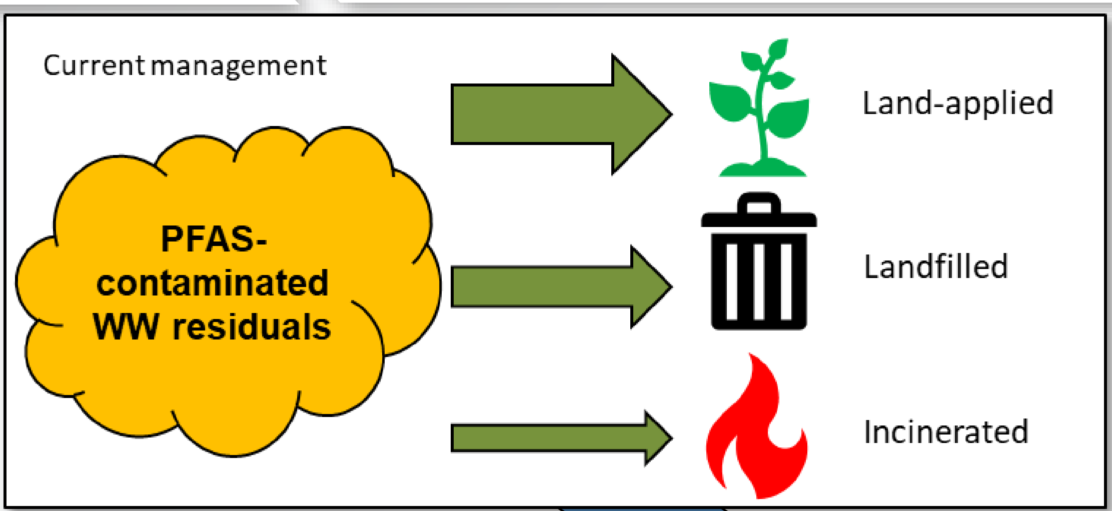
Wednesday, December 11, 2019

As the United States Environmental Protection Agency ("EPA"), Congress, and state regulatory agencies continue to push forward with per-and polyfluoroalkyl substances ("PFAS") regulations, the Maine Department of Environmental Protection has taken a bold stance regarding PFAS and the land application of biosolids. In a March 22, 2019 memorandum, the Acting Director of Maine's Bureau of Remediation and Waste Management, announced the State's decision to screen biosolids for perfluorooctanesulfonic acid ("PFOS") and perfluorooctanoic acid ("PFOA") – two of the more widely known PFAS substances – to 2.5 parts per billion ("ppb") and 5.2 ppb, respectively. This decision, which required initial sampling to be completed by May 7, 2019, effectively establishes a moratorium on biosolids land application within the state unless compliance with the established thresholds can be satisfied. With the standard set, will other states follow suit?

https://www.natlawreview.com/article/follow-leader-maine-s-strict-stance-pfas-and-biosolids-land-application-sets-stage

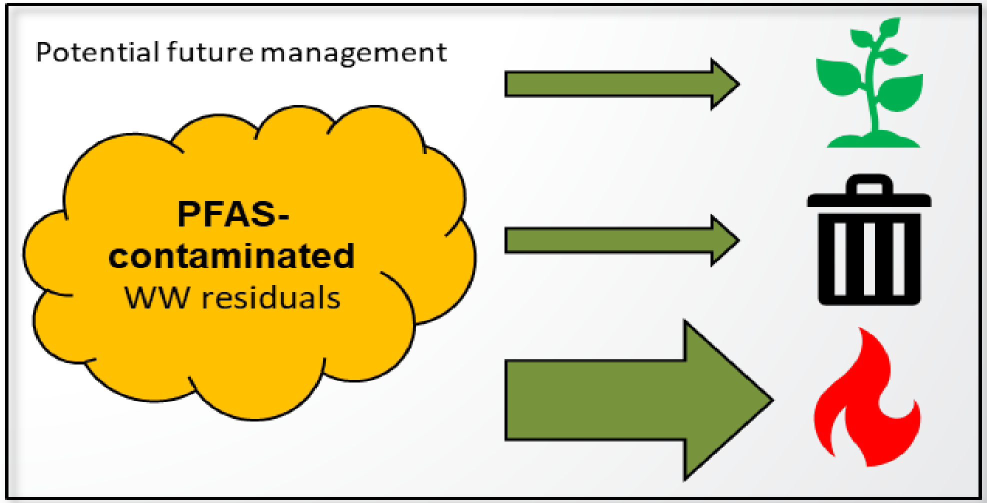
15

Changing Fate of Wastewater Residuals



USEPA is looking for partners for sampling full-scale sewage sludge incinerators

- Wastewater residual incineration may increase as policies shift to address PFAS in wastewater
- Lack data on the fate of PFAS in full-scale incinerators



Land Application of Biosolids

Goals

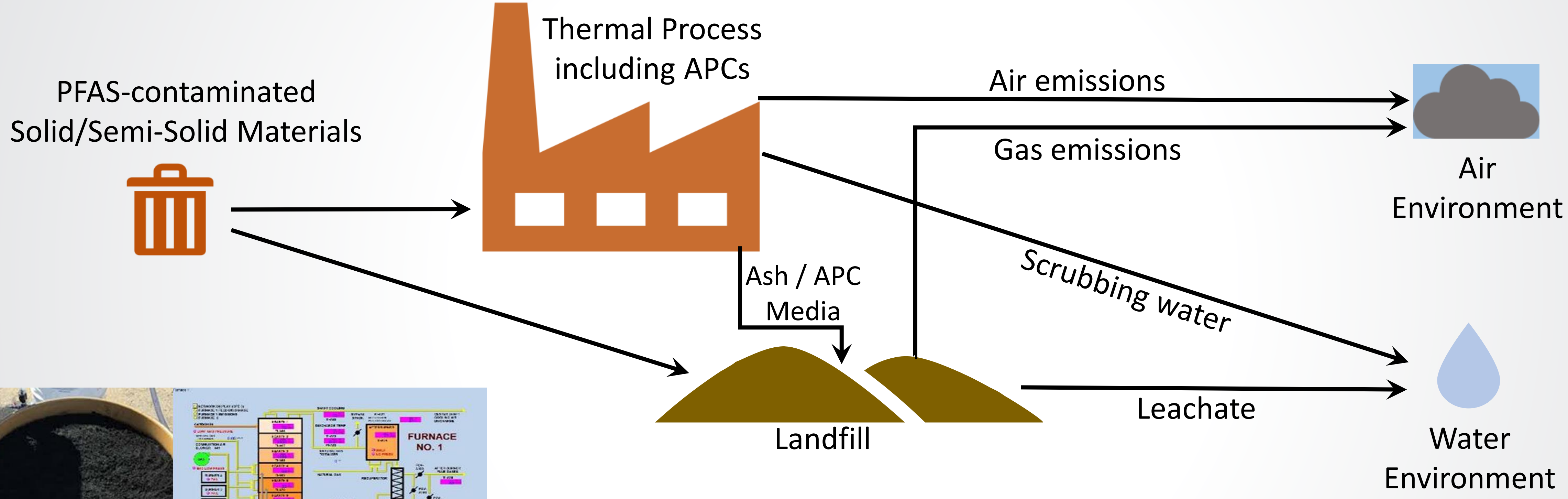
Need: Wastewater treatment conveys PFAS into the environment via residuals which are often applied as an agricultural amendment. The data gaps include:

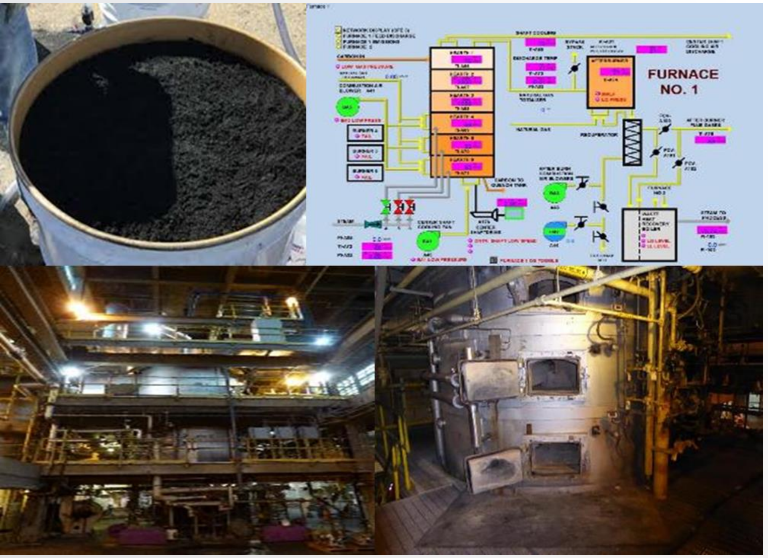
- Lack of knowledge regarding the fate of PFAS in land applied biosolids and other PFAS-containing land applied residuals
- Lack of knowledge regarding the transport of PFAS in the subsurface

Research: ORD will collect data to characterize PFAS concentrations, transport, and transformation in biosolids land application and other soil and subsurface settings

Thermal Treatment

Incineration or Thermal Reactivation





PFAS Waste Destruction and Disposal

There is a data gap regarding how the end-of-life management and ultimate disposal of PFAS-containing materials can impact PFAS concentrations in the environment.

Treatment Residuals

PFAS are found in ash, scrubbing waters, and subsequent leachates

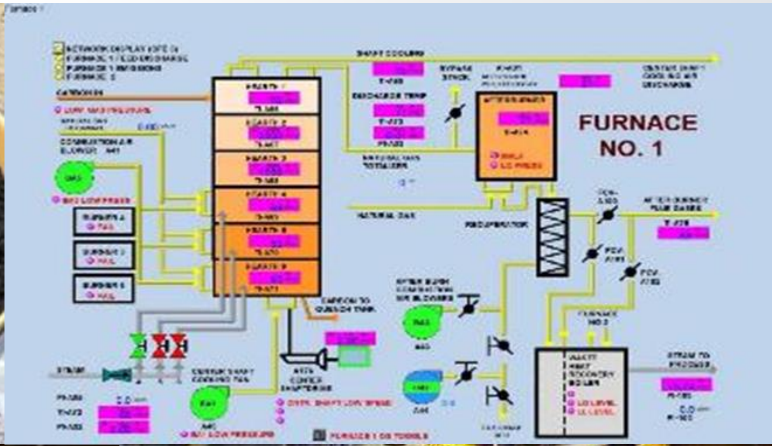
Completed, Planned, and Potential Thermal Field Studies

- R10: Soil Desorption
  - Alaska - Completed
- R9: Pyrolysis
  - Bioforce Tech - Completed
- R8: Biosolids Incineration and GAC Reactivation
  - Private lab with pilot-scale incinerators – waiting on results
- R7: Wastewater Sludge Incineration
  - Full-scale sludge incinerator – waiting on results
- R4: Municipal Solid Waste and Soil Desorber
  - Full Scale Incinerators – planning stage
- R3: WW Sludge Incineration & GAC Reactivation
  - Preliminary screening at 5 facilities – planning stage
- R2: Soil Desorber and Pyrolysis
  - In conjunction with SERDP and WRF - discussions

Granular Activated Carbon (GAC) Reactivation

Reactivation (or incineration) of spent GAC (or resin) laden with PFAS

- Site: Hazen Research Inc.
  - Private lab with pilot-scale thermal systems
  - Completed: waiting on results
- Searching for full-scale GAC reactivation facility
- Searching for opportunity with spent resin



Spent Resin: Cement Kiln Incineration

Cement kilns are operated under different operating conditions

- Gas temperatures of up to ~2,000 °C
- Gas residence times of up to 10 seconds
- Solid residence time of up to 30 minutes

EPA is actively looking for partners for sampling of cement kiln incinerators

Source: [Purolite presentation and case study. F. Boodoo et al.]

Novel Technologies (non Thermal)

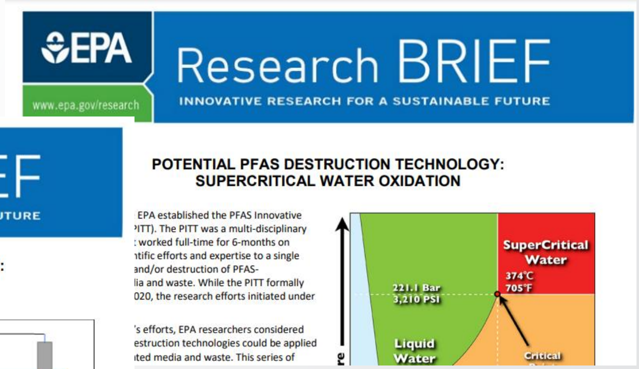
Approach for Evaluation of Technologies

- Need to supply enough energy to break carbon-fluorine bond
- Combustion may be able to do this BUT very energy intensive
- Are there more efficient ways to focus energy?
- Waters/wastewaters
  - Biological processes
  - Electrochemical oxidation
  - Hydrothermal processes
    - Supercritical water oxidation (SCWO)
    - Hydrothermal liquefaction
    - Hydrothermal oxidation
    - Sub-critical water oxidation
  - Electron beam irradiation (E-beam)
  - Advanced oxidation/reductive processes
  - Membrane distillation
  - Combined systems

SCWO and Electrochemical Oxidation

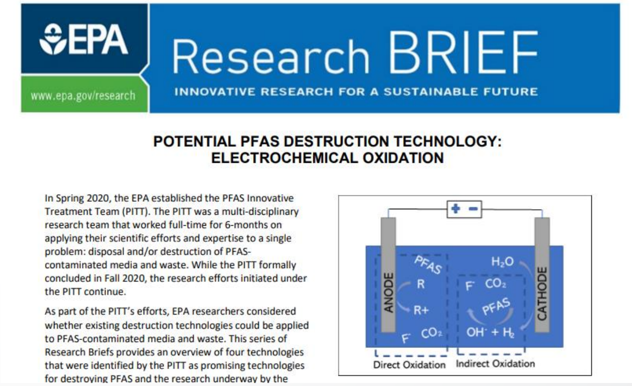
- Experiments completed
  - SCWO
    - Four case studies undertaken on AFFF
    - Published: ASCE Journal of Env. Engineering
  - Electrochemical oxidation with AECOM
    - Experiment on AFFF
    - Report being prepared
- Two Research Briefs
  - https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt

Source: General Atomics, https://www.ga.com/hazardous-waste-destruction



EPA
www.epa.gov/research
Research BRIEF
INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

POTENTIAL PFAS DESTRUCTION TECHNOLOGY:
SUPERCRITICAL WATER OXIDATION



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Research BRIEF
INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

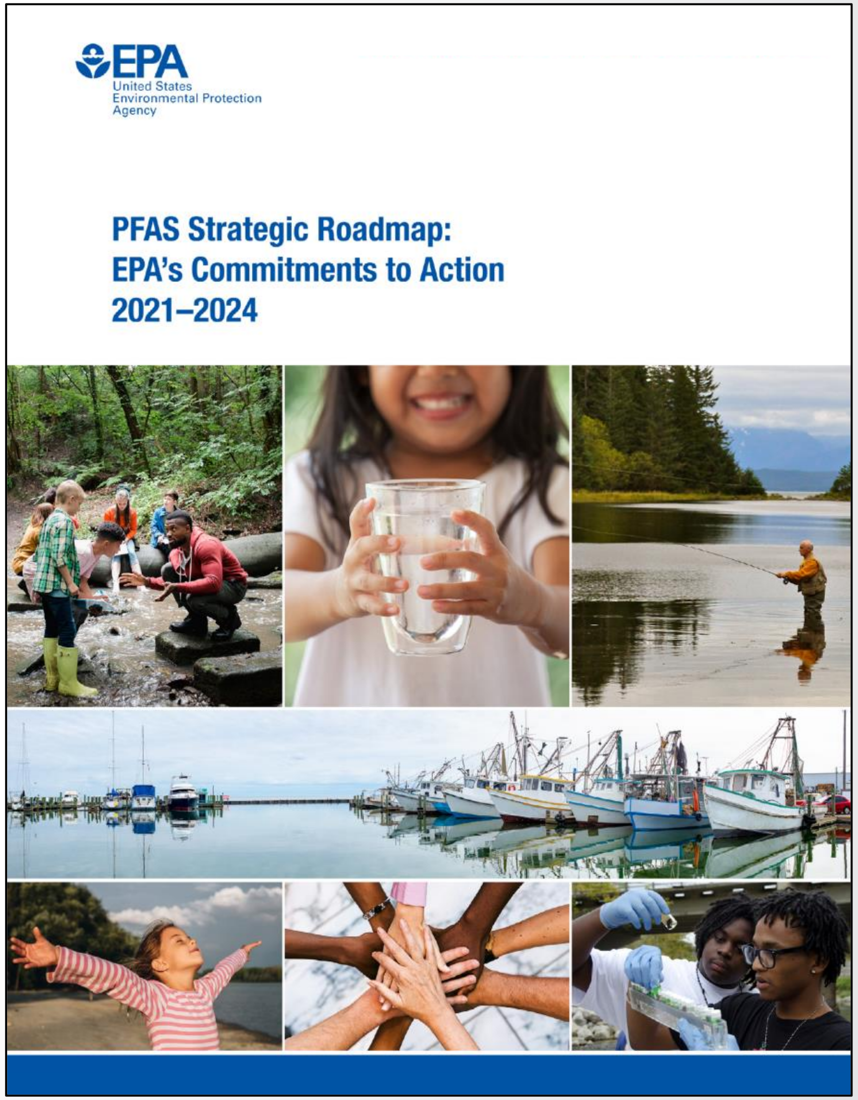
POTENTIAL PFAS DESTRUCTION TECHNOLOGY:
ELECTROCHEMICAL OXIDATION

In Spring 2020, the EPA established the PFAS Innovative Treatment Team (PITT). The PITT was a multi-disciplinary research team that worked full-time for 6-months on applying their scientific efforts and expertise to a single problem: disposal and/or destruction of PFAS-contaminated media and waste. While the PITT formally concluded in Fall 2020, the research efforts initiated under the PITT continue.

As part of the PITT's efforts, EPA researchers considered whether existing destruction technologies could be applied to PFAS-contaminated media and waste. This series of Research Briefs provides an overview of four technologies that were identified by the PITT as promising technologies for destroying PFAS and the research underway by the

EPA PFAS Strategic Roadmap

- Released October 2021
- Presents EPA's whole-of-agency approach to protect public health and the environment from the impacts of PFAS
- Focused on three goals:
  - Research
  - Restrict
  - Remediate
- Available at https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024

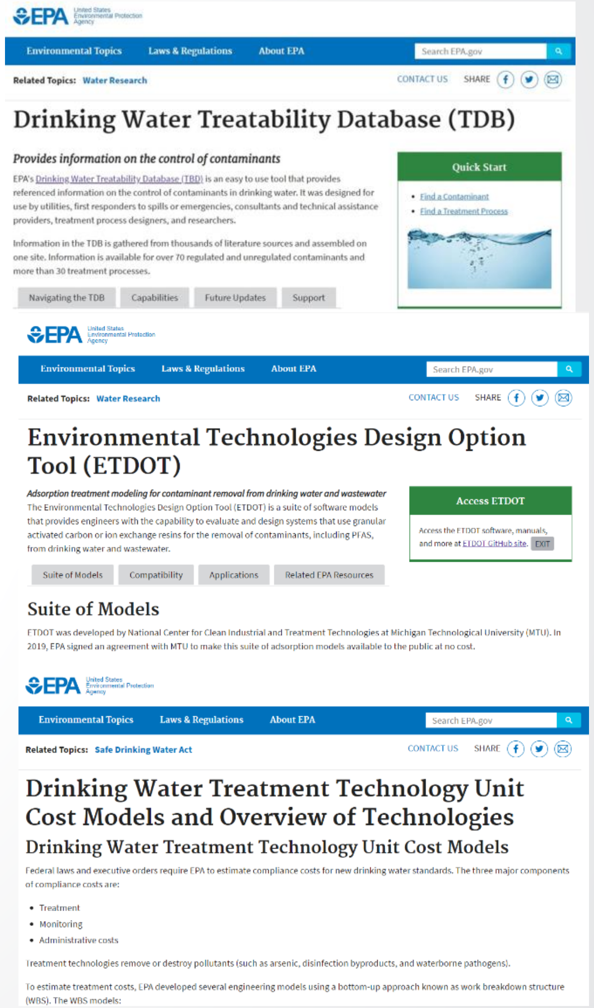


Databases and Tools

Provide tools and approaches to accurately predict the performance and cost of treating PFAS in waters

Model Scenarios

- Variable source waters
- Variable PFAS concentrations in source waters
- Alternate treatment goals
- Changing production rates
- Document secondary benefits
- Different reactivation/disposal options



[Drinking Water Treatability Database](#) or search EPA TDB
[Environmental Technologies Design Option Tool Models](#) or search EPA ETDOT
[Drinking Water Treatment Cost Models](#) or search EPA WBS

Thermal Treatment Database

- The PFAS Thermal Treatment Database (PFASTT) is a growing database that contains over 2,000 records of 80 sources documenting the treatability of PFAS in different media via various thermal processes.
- The PFASTT was created as a response to the need for a centralized database to record reliable references for researchers and general public.
- Sources cited in the database include peer reviewed and non-peer reviewed journals, government reports, conference reports, and other types of publications.

Focuses on…

- Calcining
- Granular activated carbon reactivation
- Gasification
- Hydrothermal
- Incineration
- Indirect thermal desorption
- Pyrolysis
- Smoldering

https://pfastt.epa.gov/

Reference

- Author
- Publication year
- Source
- Reference type

Scope

- Treatment process
- Scale (lab, pilot, full)
- Matrix treated (e.g., soil, sludge)

Condition

- Temperature
- Time
- Other details (e.g., atmosphere, amendments)

Results

- Analyte
- Effectiveness
- Initial concentration
- Post-treatment concentration
- Off-gas concentration
- Additional details

Questions?

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The views expressed in this presentation are those of the individual author and do not necessarily reflect the views and policies of the US EPA.

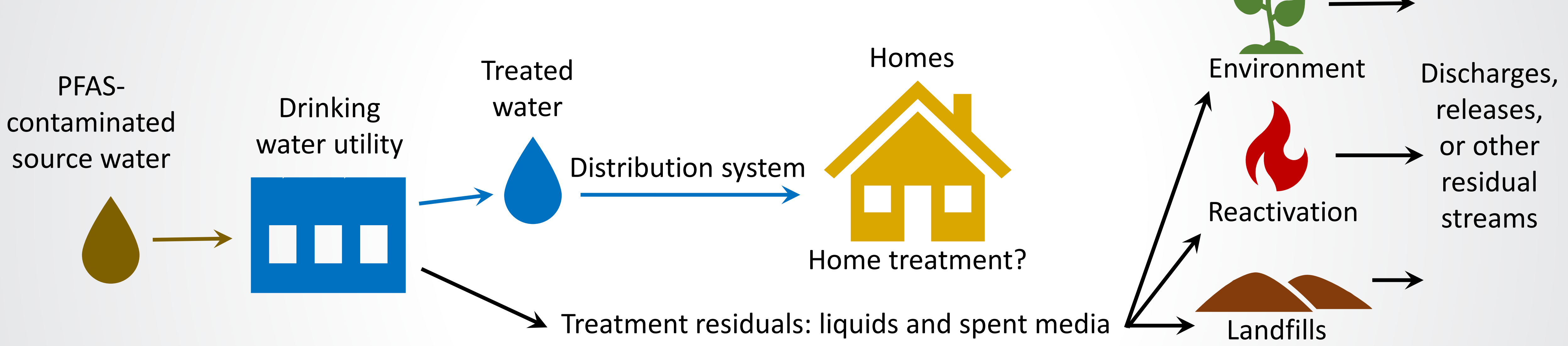
EPA PFAS Activities – www.epa.gov/pfas

PFAS Research and Development – www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

Extra slides

Drinking Water Treatment

How do we remove PFAS from drinking water?



<u>Effective Treatment Technologies for PFAS</u>

- Anion exchange resin, granular activated carbon (GAC), and membrane separation (RO) are generally effective at removing PFAS
- More effective for long-chain than short-chain PFAS
- Removal efficiencies and cost depend on source water characteristics and water system characteristics

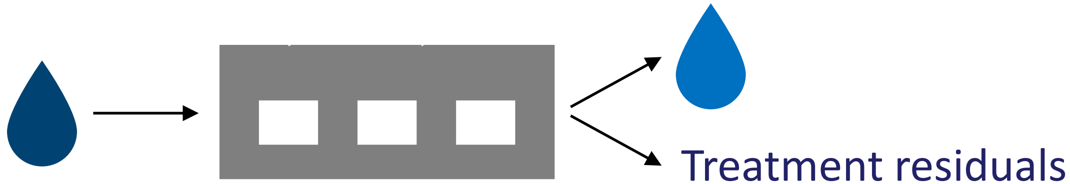
<u>Treatment Residuals</u>

- PFAS found in spent GAC and spent resin
- Spent media can be regenerated, landfilled, or incinerated with unknown releases of PFAS
- There are no known commercial treatments (mineralization) for RO concentrate streams or regenerant solutions

Risk Management

Water Treatment

Goal: Remove or reduce PFAS in drinking water and wastewater



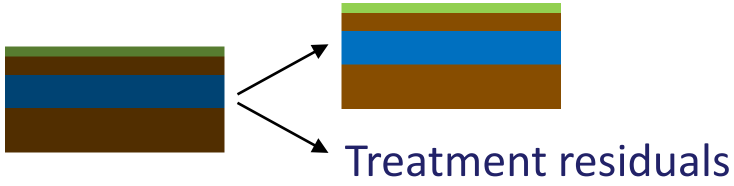
Example Technologies

Drinking water – Granular activated carbon (GAC), ion exchange resin (IX), reverse osmosis (RO)

Wastewater – Sedimentation/partitioning, GAC

Site Remediation

Goal: Remove or reduce PFAS at contaminated sites (e.g., in soil, sediment, groundwater)

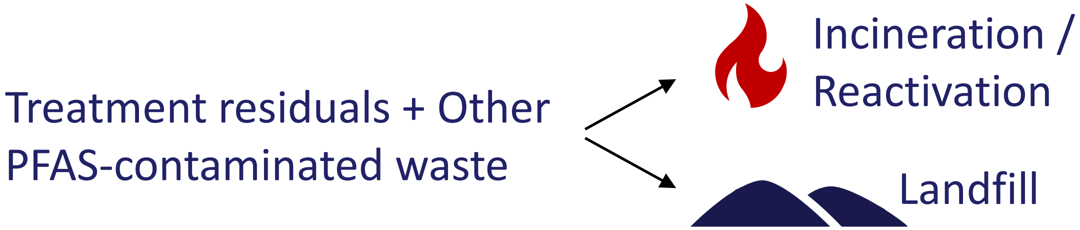


Example Technologies

Soil excavation, stabilization, pump and treat (GAC, IX, RO)

Destruction and Disposal

Goal: Prevent re-introduction of PFAS into the environment through destruction or containment



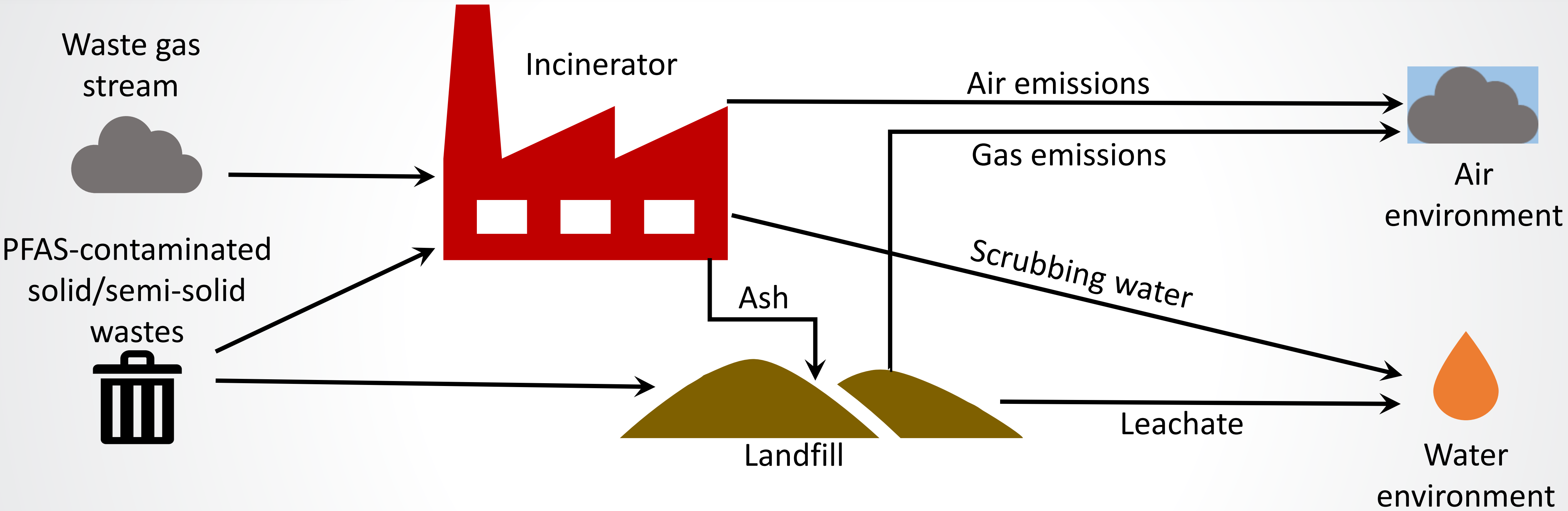
Example Technologies

"Conventional" – Incineration, GAC reactivation, landfilling

"Innovative" – Supercritical water oxidation, pyrolysis/gasification, electrochemical oxidation, etc.

Waste Management

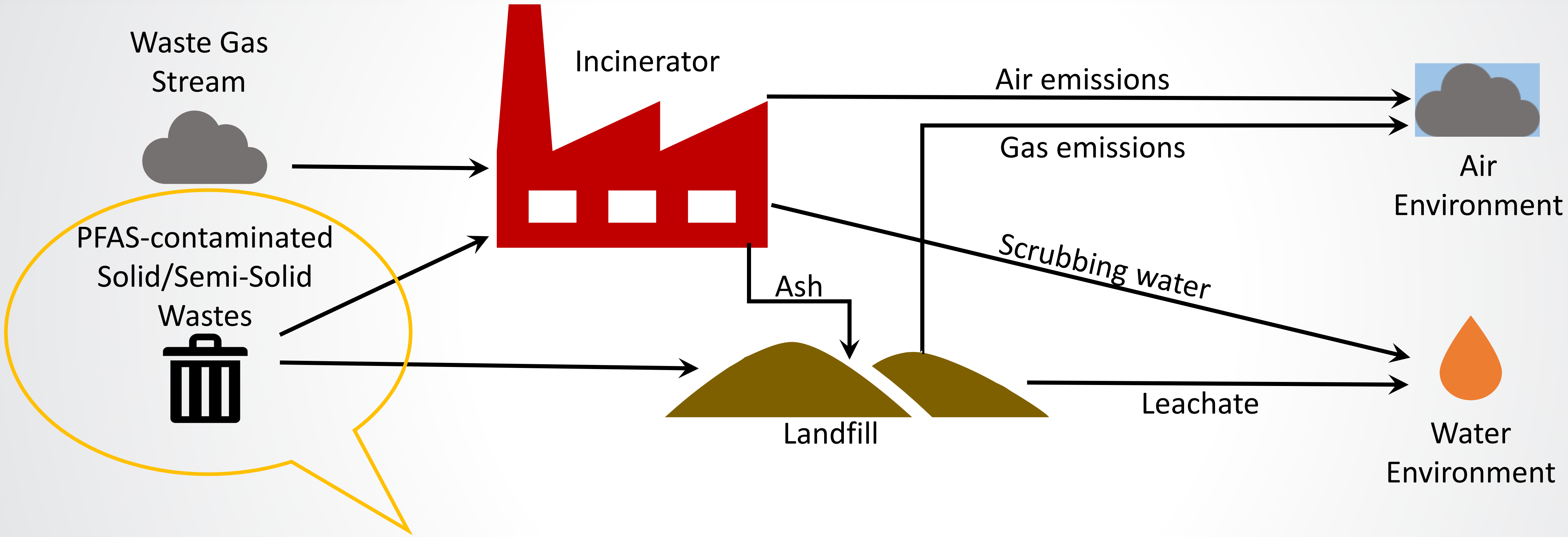
Destruction and Disposal



PFAS Waste Destruction and Disposal

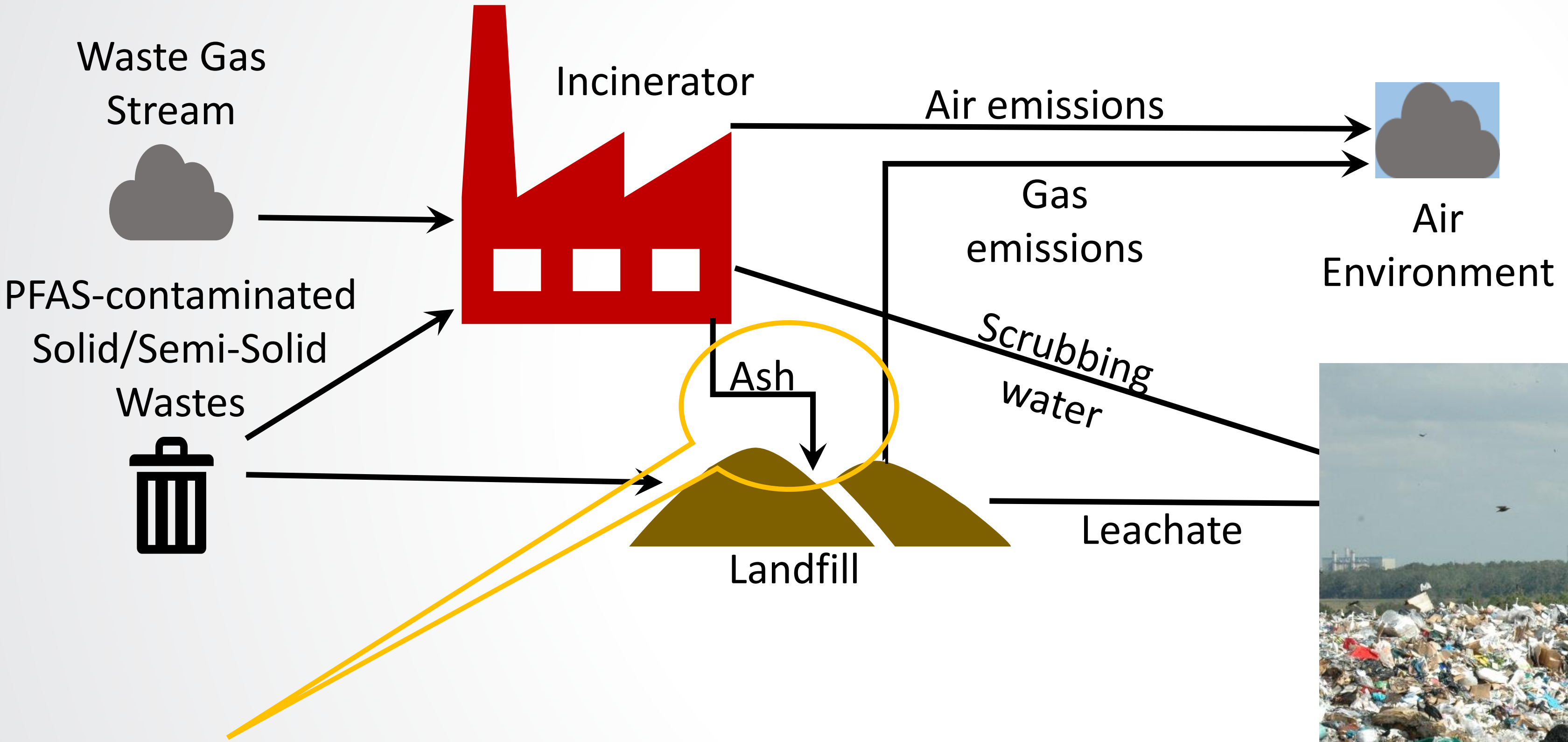
- Data gap in the understanding of PFAS behavior during end-of-life management and ultimate disposal
- Some management approaches may release PFAS into the environment
- Evaluate efficacy of disposal/destruction technologies for solid and semi-solid wastes (e.g., landfilling, incineration, in situ stabilization) to manage end-of-life disposal
- Evaluate the treatment of waste gas streams and the emissions from those thermal oxidizers
- Evaluate possibility of products of incomplete combustion/destruction

Approach



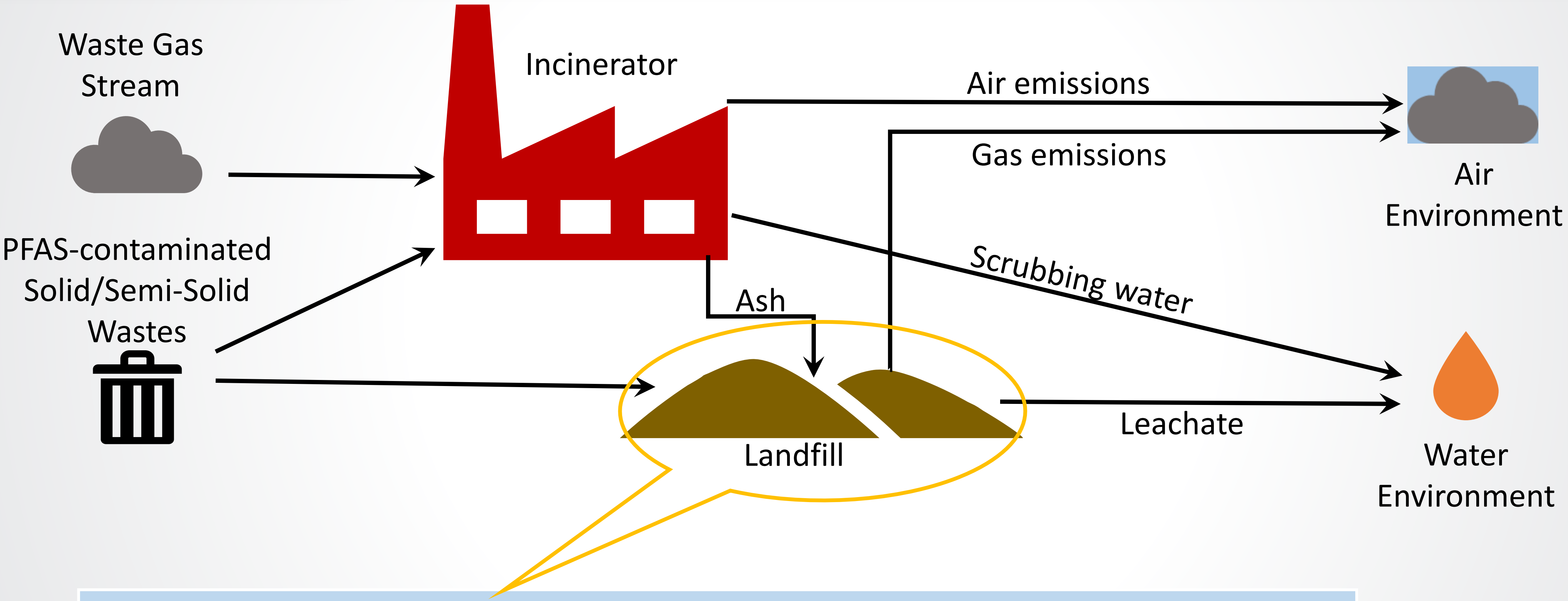
- PFAS in fresh waste vs. landfilled waste
- Evaluating PFAS waste solidification techniques for PFAS immobilization
- Mobility of PFAS from waste utilizing the Leaching Environmental Assessment Framework (LEAF)

Approach



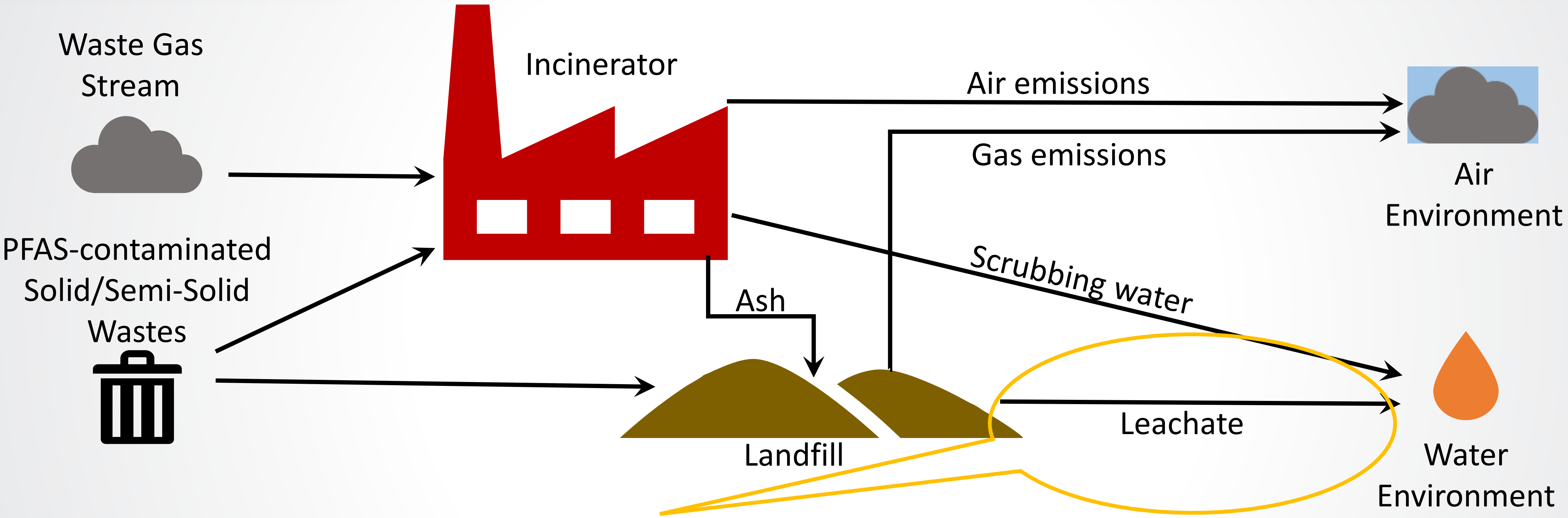
- Quantify PFAS content of MSW incinerator ash
- Evaluate the mobility of PFAS from incinerator ash

Approach



- Demonstrate PFAS transformation is conducive in landfill environment (i.e., decomposition, elevated temperatures, low oxygen, and prolonged contact time)
- Examining the transport of PFAS compound through landfill liners
- PFAS leaking though primary liner system

Approach



- Quantifying PFAS in landfill leachate
  - Municipal solid waste landfills, construction and demolition landfills, ash monofils, and hazardous waste landfills
- Evaluating the effectiveness of conventional leachate treatment for the removal of PFAS
- PFAS emissions during landfill leachate treatment (e.g., volatilization, constructed wetlands)