Occurrence of Per- and Polyfluoroalkyl Substances (PFAS) in New Hampshire Biosolids

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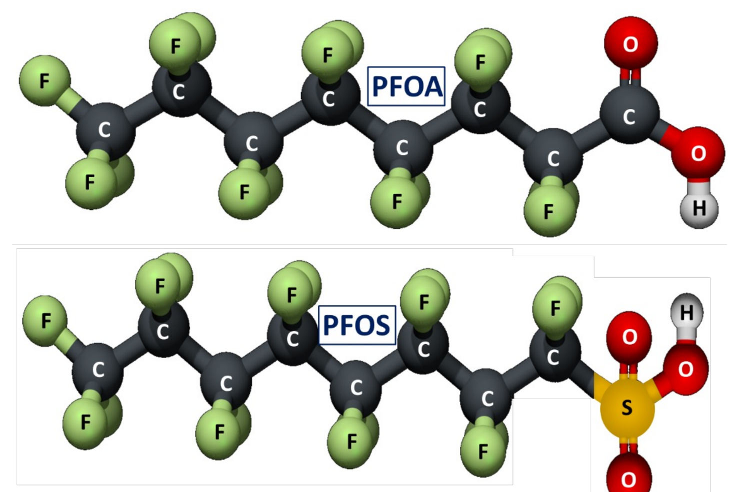
Background

- PFAS: group of over 4,000 compounds
- First synthesized in 1940s and found in:
  - Aqueous film forming foams
  - Stain repellents
  - Food wrappers
  - Waterproof clothing
  - Many other waterproof and/or nonstick products
- Structure: Long carbon-fluorine chains
  - Highly resistant to biodegradation
  - Chemically & thermally stable
  - Fluorinated end is lipophobic and hydrophobic



Source: Vigdor & Londergan

Figure 1: Chemical structure of PFOA and PFOS, two common PFAS.

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-Chain PFCAs				Long-Chain PFCAs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA*	PFNA*	PFDA	PFUnA	PFDoA
PFSAs	PFBS*	PFPeS	PFHxS*	PFHpS	PFOS*	PFNS	PFDS	PFUnS	PFDoS
	Short-Chain PFSAs		Long-Chain PFSAs						

Table 1: PFAS classifications and names based upon carbon chain length and classification as PFCA (perfluoroalkyl carboxylic acid) or PFSA (perfluoroalkyl sulfonic acid). Compounds denoted with [*] were specifically targeted in this investigation. Table modified from Sanborn, Head, & Associates.

- Pose significant threat to human health and the environment
- March 14, 2023: EPA proposes national drinking water standard for 6 PFAS

PFOA, PFOS	4 parts per trillion (ppt)
PFNA, PFHxS, PFBS, GenX	Proposed Hazard Index to determine if combined PFAS levels pose risk

- Biosolids created at wastewater treatment facilities can be a source of PFAS contamination

Source: Interstate Technology and Regulatory Council

Figure 2: Diagram showing potential sources of PFAS to surface and groundwater resulting from activity at wastewater treatment facilities and landfills.

Motivation and Research Objectives

- PFAS from industrial processes and consumer items is present in wastewater
- Wastewater treatment and processing creates post-consumer products such as compost, sludge, and ash.
- While highly resistant to degradation overall, some PFAS , known as precursors degrade to other PFAS (terminal products).
- Understanding the specific PFAS present in biosolids that undergo different processing methods can help to understand chemical transformation of PFAS.
- Land applied biosolids have caused significant PFAS contamination issues in Maine and other locations.
- New EPA proposed drinking water standards are highly stringent. Further concrete data may point out lack of feasibility.

OBJECTIVES

- To determine the diversity of different PFAS species present in wastewater biosolid products in the state of New Hampshire and track this diversity over time
- To determine potential differences in molar concentration across different biosolids processing methods
- To determine changes in concentrations of PFAS in biosolids samples over time.

Methodology

PROCESSING GROUP DESIGNATIONS

Eight groups were defined based on processing methods used to create biosolids products (n=99):

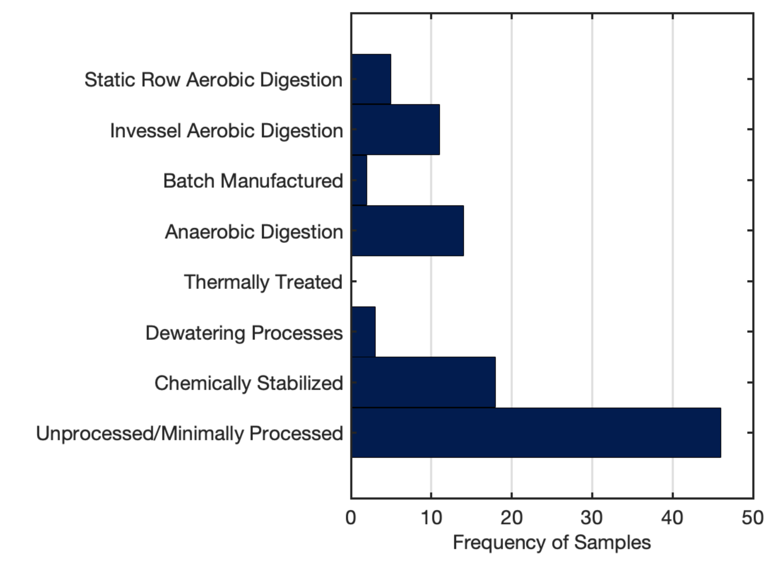


Figure 3: Frequency histogram showing processing methods for the 99 samples used in statistical analysis. The most common processing method was 'Unprocessed/Minimally Processed'; this includes products such as sludge, short paper fiber and drinking water treatment cakes. There were no thermally treated samples (e.g., incinerator ash) that were suitable for statistical analysis, but there were multiple present in the original dataset.

PRELIMINARY DATA FILTERING

Data provided from New Hampshire Department of Environmental Services (NHDES) included 189 biosolids samples collected from 2017-2022.

The raw dataset was subjected to the following preliminary filtering steps:

- Removal of 2017-2018 data for ensured consistent sampling techniques
- Removal of field and equipment blank samples
- Removal of samples lacking analytes found in other samples

Each sample was sorted into the appropriate process group.

Total of 99 samples from 28 facilities used in analysis (NH = 22, ME = 1, MA = 1, NY = 2, VT = 2).

STATISTICAL ANALYSIS OF CONCENTRATION DATA

- Kruskal-Wallis (Rank Sums) test* for variation in concentrations of EPA targeted PFAS between processing groups
- Wilcoxen test* for variation between pairs of processing groups for PFAS that did show variation

*All statistical tests assume non-normal distributions and were conducted using JMP Pro 16.

Results

PRELIMINARY DATA VISUALIZATION

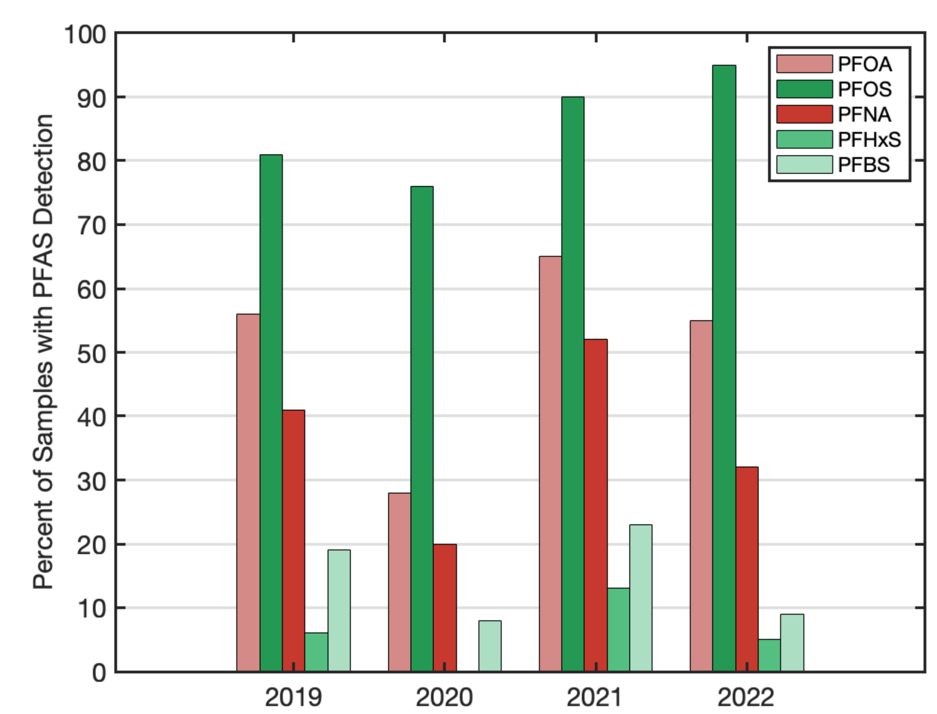


Figure 4: Percent detection of PFAS in all samples from 2019-2022.

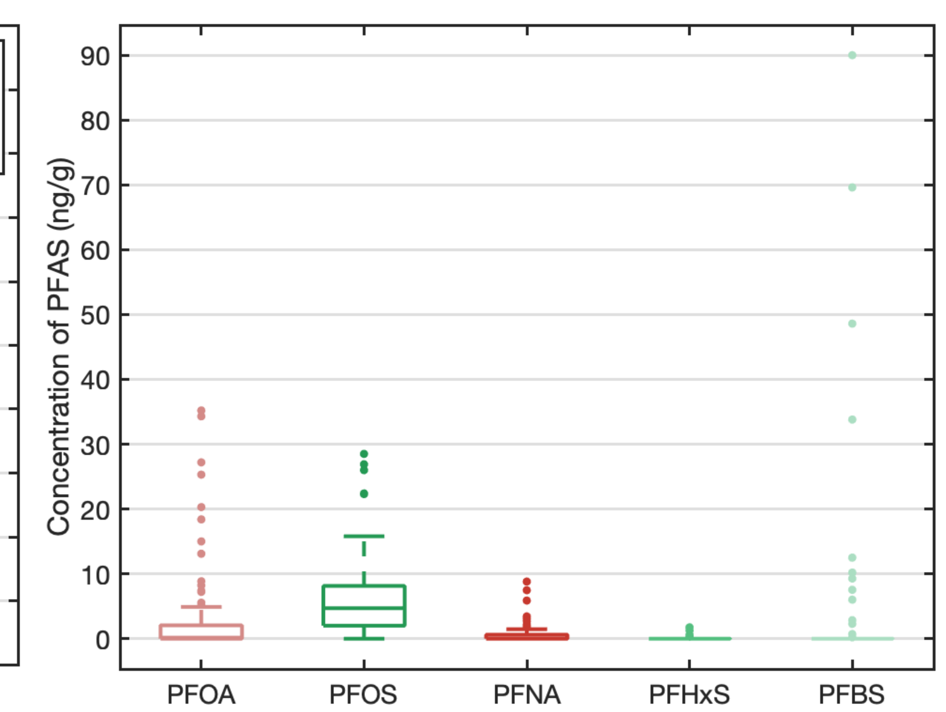


Figure 5: Distributions of PFAS concentration for all samples from 2019-2022 for five of the six PFAS targeted by the EPA proposed drinking water standards.

KEY FINDINGS

- PFOS consistently detected the most frequently
  - Detected above RL in 76 to 95% of samples
- PFHxS detected with lowest frequency
  - Detected above RL in 0 to 13% of samples
- PFBS had greatest range in concentration values
  - Highest concentration: 90 ng/g
- PFOS had greatest median concentration; 4.7 ng/g
- PFOA, PFNA, PFBS, and PFHxS concentrations are not equal across all processing groups. PFOS had no detectable difference in concentration across the aggregate of all eight processing groups.
- Invessel Aerobic Processing was the most common processing method to produce PFAS with significantly different (greater) concentrations than other methods.

STATISTICAL ANALYSIS OF CONCENTRATION DATA

	PFOA	PFOS	PFNA	PFBS	PFHxS
Chi Square Test Statistic	32.1029	11.6665	26.7305	57.709	22.0413
Prob > Chi Square	<0.0001	0.0698	0.0002	<0.0001	0.0012

Table 3: Results of Kruskal-Wallis test to determine if there is a difference in central tendency of concentration of each PFAS between processing groups.

Process A	Process B	p-value			
		PFOA	PFNA	PFBS	PFHxS
Invessel Aerobic Processing	Chemically Stabilized	0.0001	0.0003	<0.0001	0.0184
Invessel Aerobic Processing	Anaerobic Digestion	<0.0001	<0.0001	<0.0001	0.1932
Invessel Aerobic Processing	Dewatering Processes	0.0092	0.0049	0.0384	0.0449
Invessel Aerobic Processing	Batch Manufactured	0.0127	0.0286	0.1366	0.3988
Batch Manufactured	Anaerobic Digestion	0.1752	0.2475	0.0140	0.4576
Static Row Aerobic Processing	Anaerobic Digestion	0.0425	0.3744	0.1202	0.2217
Static Row Aerobic Processing	Invessel Aerobic Processing	0.1037	0.0275	0.0146	0.0242
Unprocessed/Minimally Processed	Batch Manufactured	0.0731	0.0394	0.0018	0.0001
Unprocessed/Minimally Processed	Invessel Aerobic Processing	<0.0001	<0.0001	<0.0001	<0.0001

Table 4 : Selected results of Wilcoxen test for pairs to determine potential differences between central tendency of PFAS concentration between each set of processing groups for PFAS in Table 3 that showed differences between at least two group. This reduced table only includes pairs of groups that showed a statistically significant difference in score mean rank.

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