The Cycle of PFAS and its Evolving Landscape

Northeast Recycling Council PFAS Webinar

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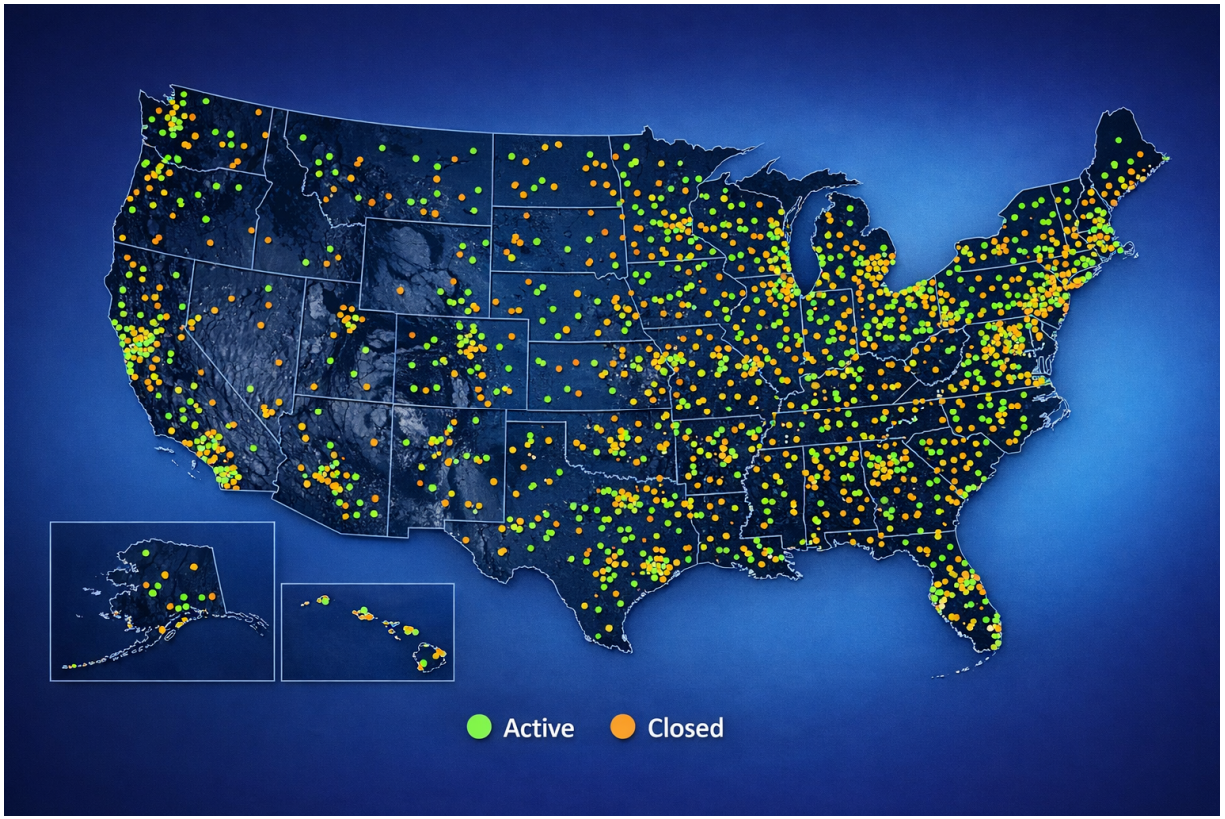
PFAS in the Waste Infrastructure

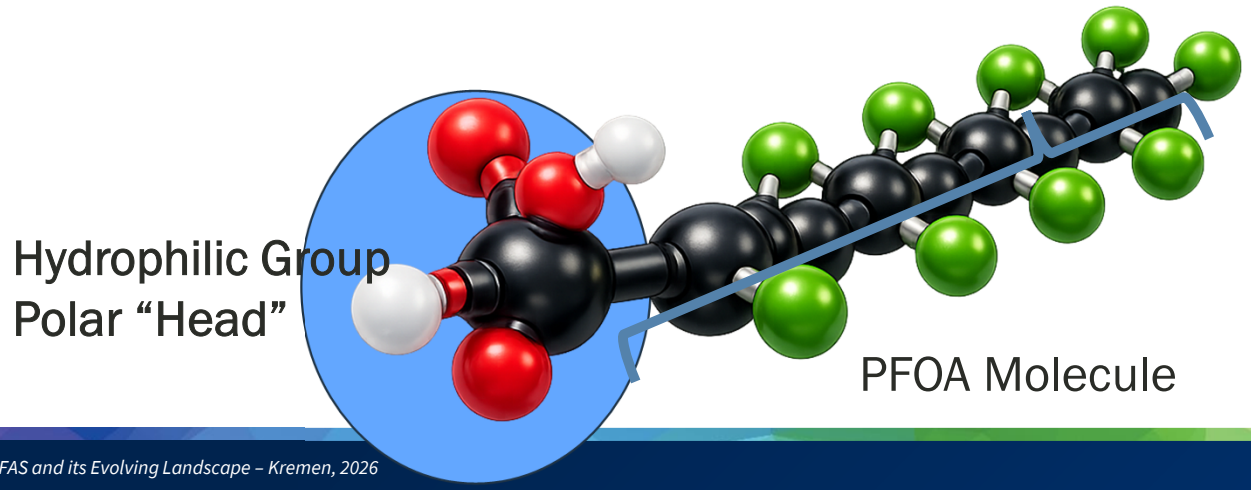
Geographic Distribution of MSW Landfills



Source:
US EPA Landfill Methane Outreach Program (LMOP). Dataset includes approx. 2,600 MSW landfills; representing the majority of US Subtitle D landfills.

Per- and Polyfluoroalkyl Substances (PFAS)

- Ubiquitous use as surfactants
- Bio-accumulative
- Evidence for adverse health impacts
- Widely present in the environment
- Resilient to treatment
- Low adsorption to soil/sediments
- Evolving regulatory environment



Common Single Bonds	Average Bond Energy (kJ/mol)
H-F	*565*
C-F	*485*
H-O	459
Si-O	452
H-H	432
H-Cl	428
H-Br	362
⋮	⋮
N-F	283
C-S	272
N-Br	243
Si-Si	22
C-I	213
N-O	201
P-P	201
N-N	167

Source: *Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).*

Conservation of Mass

Mass is neither created nor destroyed
it can only be transferred, transformed, or accumulated within a system.

Defined control volume is essential
mass conservation applies only after clearly specifying system boundaries and interfaces.

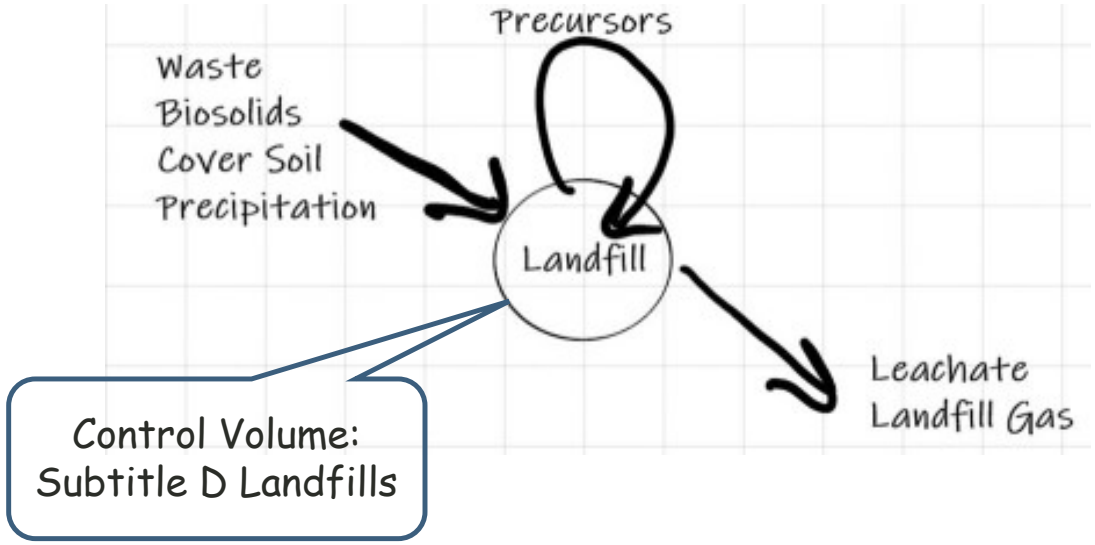
Balance of inputs, outputs, and internal generation
changes in stored mass equal mass in minus mass out plus/minus internal generation or conversion.

Applies across all scales and phases
valid from molecular to system scale and for solids, liquids, and gases.

Rates of change matter more than totals for dynamics
temporal changes are more meaningful than absolute mass

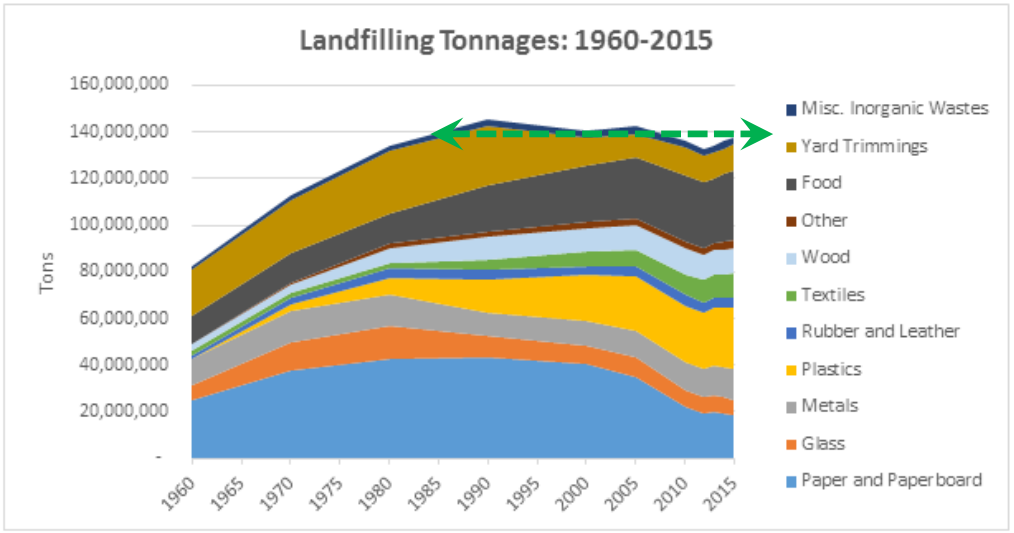
PFAS Mass Balance in Landfills

$$\begin{bmatrix} PFAS\ in \\ Landfills \end{bmatrix} = \begin{bmatrix} Landfilled \\ PFAS \end{bmatrix} - \begin{bmatrix} PFAS \\ leaving\ Landfills \end{bmatrix} + \begin{bmatrix} Precursors \\ converted\ into\ PFAS \end{bmatrix}$$



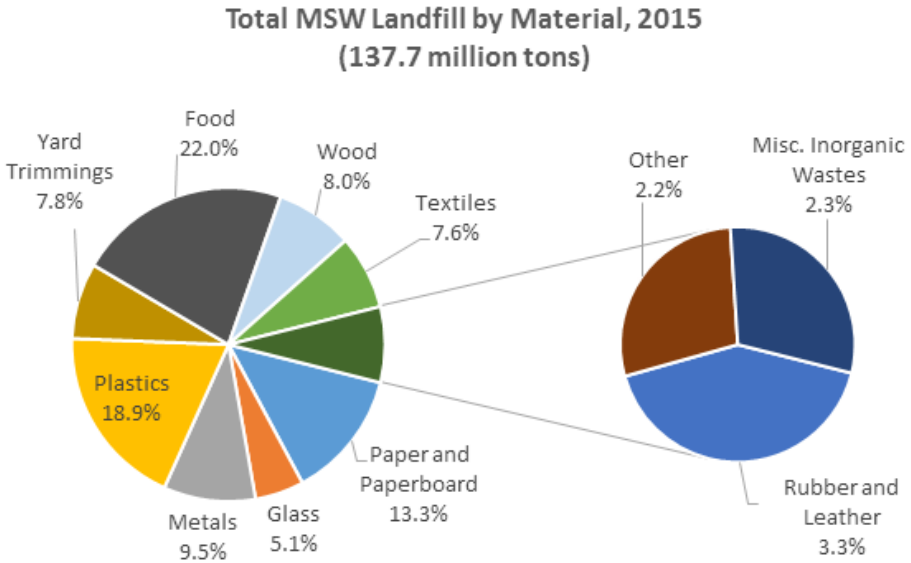
$$\begin{bmatrix} Rate\ of \\ Accumulation \end{bmatrix} = \begin{bmatrix} Rate \\ in \end{bmatrix} - \begin{bmatrix} Rate \\ out \end{bmatrix} + \begin{bmatrix} Rate\ of \\ Generation \end{bmatrix}$$

Landfilled MSW Tonnage & Composition



Source: USEPA (2018)

Annual tonnages stagnate at about 140M tons for the last ±20 years.



MSW PFAS Content

- MSW typically not analyzed for PFAS content
- Challenging sampling matrix
- Analytical methods in flux
- Limited published data for select waste components
- Dual track:
  - Order-of-Magnitude Estimate
  - Published data

Challenging Sampling and Analytical Matrix

Order-of-Magnitude Estimate

MSW PFAS content (assumed)	PFAS Mass landfilled
1 ng/g	124.9 kg/yr
10 ng/g	1,249.2 kg/yr
100 ng/g	12,492 kg/yr
1,000 ng/g	124,920 kg/yr

PFAS in MSW

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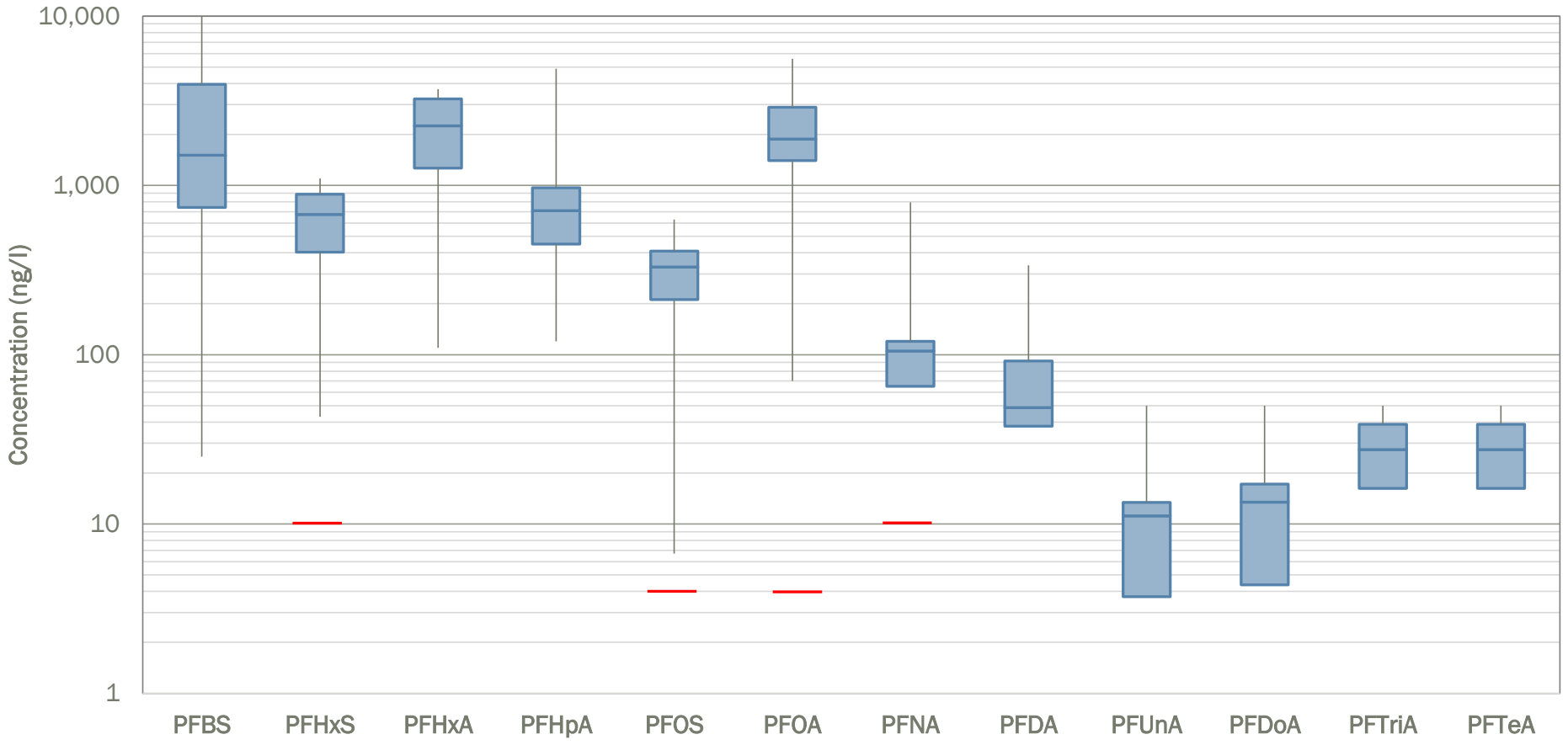
Fraction	Disposal (Mtons)	PFAS Content (ng/g)	Source	PFAS Mass (kg/yr)
Food	27.73	27.7 – 37.4	Choi et al., 2019	1,040 – 1,400
Wood	11.02	11.0 – 29.4	Wood Sealants	110 – 325
Textiles	10.13	21.5 – 365	Apparel & Membranes	210 – 3,695
Other	2.66	78.6 – 395	Misc. Products	210 – 1,050
Organic Waste	2.91	10 – 1,000	Estimate	30 – 2,915
Rubber & Leather	4.43	10 – 1,000	Estimate	45 – 4,435
Paper, Paperboard	16.6	10 – 225	Food Contact Paper	165 – 3,710
Glass	6.21	10 – 1,000	Estimate	62 – 620
Metals	12.54	10 – 100	Estimate	125 – 1,255
Plastics	24.32	10 – 100	Estimate	245 – 2,431
Yard Trimmings	7.85	37.4 – 44	Choi et al., 2019	295 – 350
Totals	126.64			2,327 – 22,186

Equivalent Concentration Range: 20 - 180 ng/g

Typical Leachate PFAS Concentrations



Source: Tetra Tech (2018 – 2026)

USEPA National Primary Drinking Water Standards (May 14, 2025)

PFAS Released with Leachate

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National Release Potential (Lang et al., 2017)

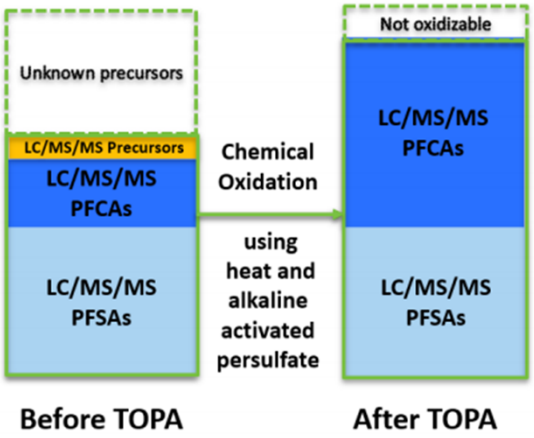
Climate	Wet		Temperate		Arid	
Landfill Age	<10 yr (n=14)	>10 yr (n=12)	<10 yr (n=2)	>10 yr (n=6)	<10 yr (n=2)	>10 yr (n=4)
ΣPFAS (ng/l)	15,000	11,000	7,000	11,000	29,000	15,000
	±16,000	±12,000	±1,000	±9,000	±1,000	±16,000
Leachate	12,700 Mgal/yr		3,450 Mgal/yr		30 Mgal/yr	
Loading	625.0 kg/yr		117.5 kg/yr		2.5 kg/yr	
Leachate	**16,180 Mgal/yr**					
ΣPFAS	**745.0 (kg/yr)**					

Notes:

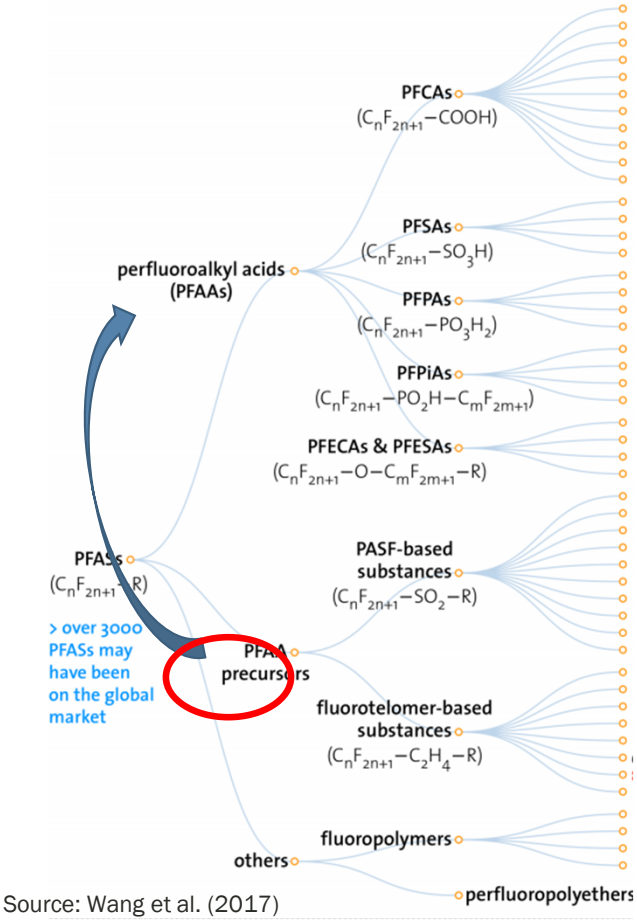
- Total of 70 quantifiable ("ΣPFAS")
- Excludes oxidizable precursors
- Estimated for averages, as standard deviations are too large

Precursors of Perfluoroalkyl Acids (PFAA)

- The PFAS class consists of
  - PFAA precursors
  - PFAA, including PFOS and PFOA
  - Others, e.g., fluoropolymers
- 'Terminal PFAS' = non-degradable PFAA
- Total Oxidizable Precursor Assay



Source: Chiang (n.d.)



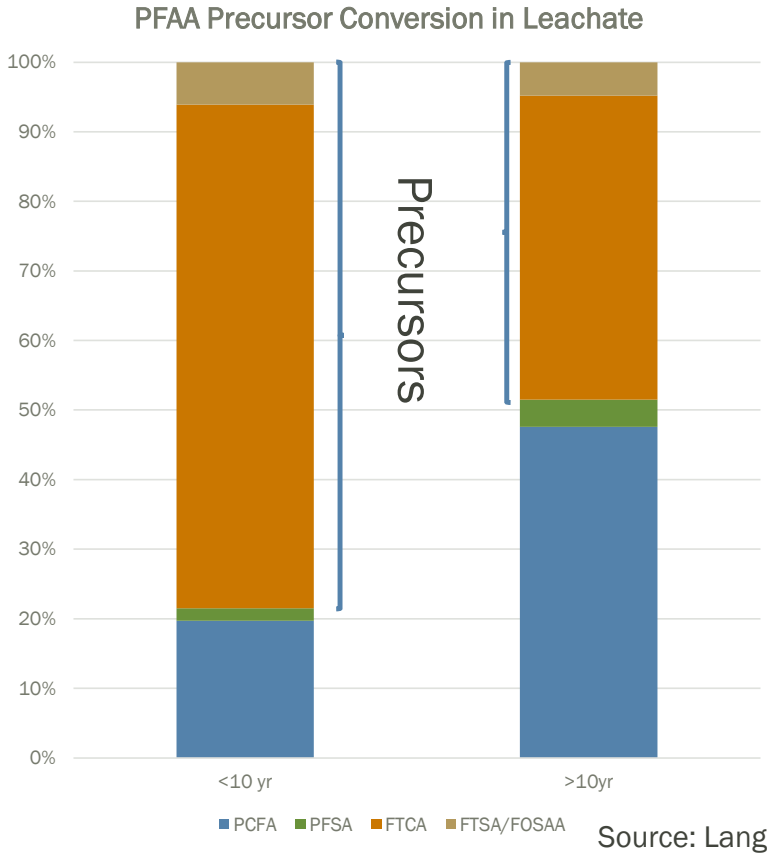
Source: Wang et al. (2017)

Leachate PFAA Precursor Estimate

- Precursor content decreased from 78.5% to 48.5% in LFs > 10 yrs
  - PFAS content is underestimated
- PFAA precursor oxidation increases leachate PFAS content
- Additional oxidation during leachate treatment
- PFAA conversion estimate:

745.0 kg/yr × 2 = 1,490 kg/yr

Factor of Safety



Source: Lang et al. (2017)

Precipitation

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Assumptions

- Precipitation is the predominant source for leachate
- PFAS in rainwater at averaged concentrations
- Leachate collection 16,180 Mgal/yr

$$16{,}180 \cdot 10^6 \frac{gal}{yr} \cdot 284.6 \frac{ng}{l} = \cdots = 17.43kg$$

Researcher	Period	Samples	Locations
Scott et al. (2006)	1998 – 2004	196	US - MD, DE, NY, VT CA – NS, BC, ON
Pike et al., (2021)	2020	7	US – OH, IN, WY

PFAS (ng/l)	'Average of Averages'
TFA	251.5
PFBA	7.6
PFPeA	5.3
PFHxA	4.3
PFOA	6.4
PFNA	4.7
PFDA	1.6
PFOS	6.7
ΣPFAS, total	284.6

How big is the Biosolids Problem?

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Biosolids Production

Disposal Method	tons/year*	Percent
Land Application	4.74 million	55%
Landfilling	1.46 million	17%
Incineration	2.41 million	28%
Total	8.61 million	100%

* 18%-20% Moisture Content

Source:
Northeast Biosolids and Residuals Association (2007)

Biosolids PFAS Content

Disposal Method	ΣPFAS (kg/year)	Percent
Land Applied	1,375 – 2,070	50% - 60%
Landfilled	470 – 590	14% - 21%
Incinerated	550 – 690	16% - 25%
Total	2,395 – 3,350	

Source:
Venkatesan & Halden (2013)

PFAS in Biosolids

Source: Venkatesan and Halden (2013)

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Compound	Concentration (ng/g-dw)	Annual PFAS Estimate (kg/yr)	
		Biosolids	Landfilled
PFBA	2.0 (1.2-3.2)	10.0-12.5	1.7-2.1
PFPeA	3.5 (1.8-6.7)	17.7-22.2	3.0-3.8
PFHxA	6.2 (2.5-11.7)	31.8-39.9	5.4-6.8
PFHpA	3.4 (1.2-5.4)	17.4-21.8	3.0-3.7
PFOA	**34.0 (11.8-70.3)**	**172-215**	**29.3-36.6**
PFNA	9.2 (3.2-21.1)	47.2-59.1	8.0-10.0
PFDA	**26.1 (6.9-59.1)**	**133.0-167.0**	**22.7-28.4**
PFUnDA	11.7 (2.8-38.7)	59.9-69.7	10.2-12.8
PFDoDA	10.9 (4.5-26.0)	55.6-69.7	9.4-11.9
PFBS	3.4 (2.5-4.8)	17.6-22.0	3.0-3.7
PFHxS	5.9 (5.3-6.6)	29.9-37.5	5.1-6.4
PFOS	**403 (308-618)**	**2,052-2,575**	**349-438**
PFOSA	**20.7 (2.2-68.1)**	**105-132**	**17.9-22.5**
ΣPFAS, total		**2,749-3,443**	**467.7-586.7**

4 PFAS ≅ 85% of PFAS by Mass

Equivalent Concentration Range: 540 (350 – 940) ng/g

PFAS in Landfill Gas

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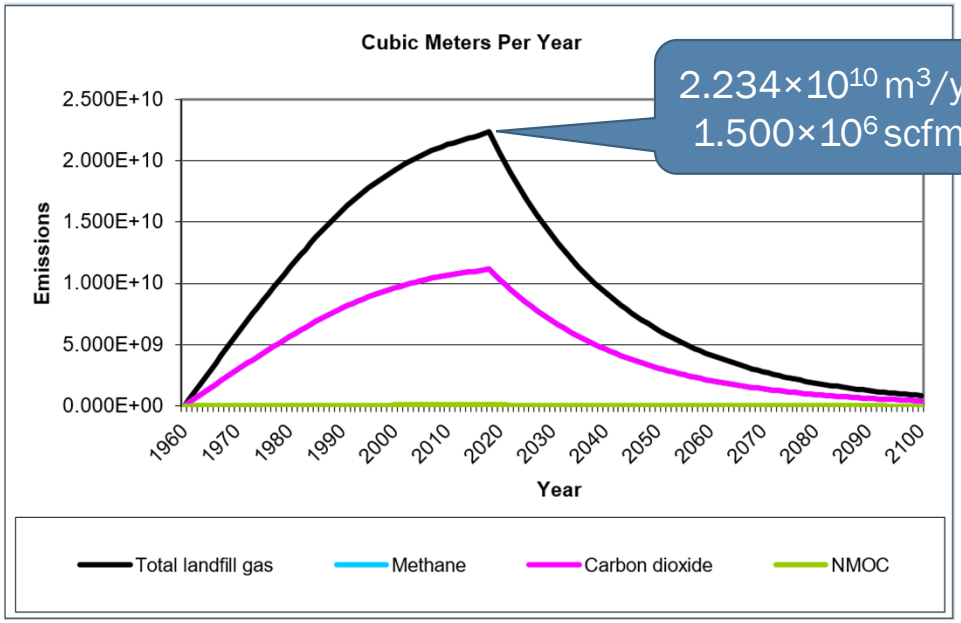
Challenges

- Estimation for LFG Generation
- Generation vs. Recovery
- No relevant published data available

Approach

- LFG Generation
  - LandGEM with national landfilled waste as input
  - LMOP published data for recoverable LFG potential
- Estimate LFG PFAS using Henry's Law

LandGEM-based Approach to LFG Generation Estimate

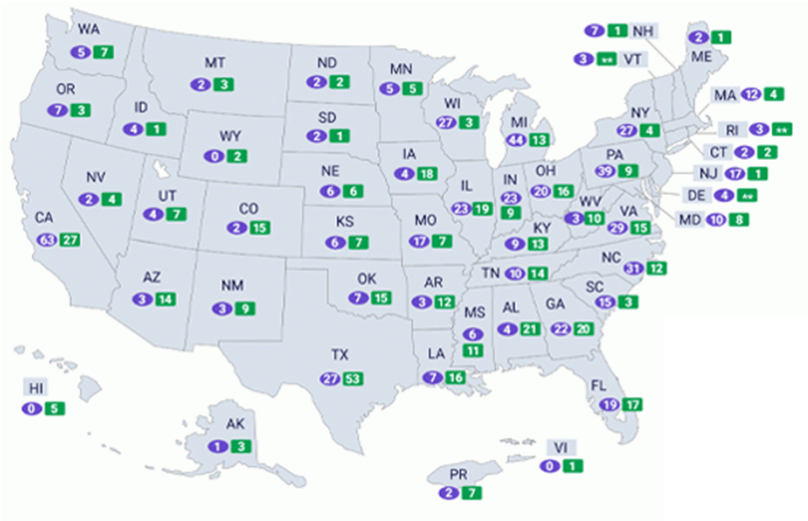


LandGEM, using 'CAA Conventional' settings:

- Methane generation rate: k=0.05 yr^{--1}
- Specific methane generation capacity: L_0=170 m^3/Mg

LMOP-based Approach to LFG Generation Estimate

LFG Recovery Potential Estimate	
Operational	334×10^6 scfd
Candidates	515×10^6 scfd
Subtotal	**849×10^6 scfd**
Collection Efficiency (assumption): 60%	
Generation	$1.,415 \times 10^6$ scfd 0.983×10^6 scfm



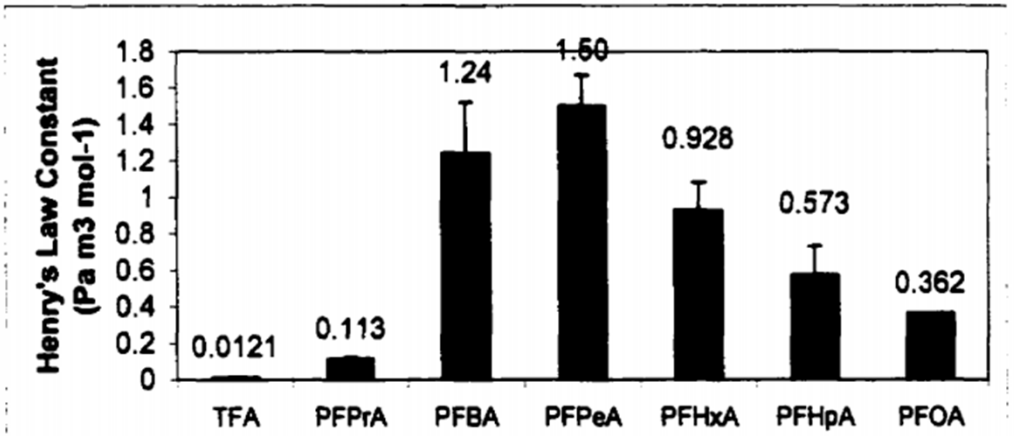
Results

	LandGEM	LMOP	Average
scfm	1.500×10^6	0.983×10^6	**1.242×10^6**
m^3/yr	2.234×10^{10}	14.635×10^9	**18.488×10^9**

Calculating PFAS in LFG

Henry's Law
and
Ideal Gas Law

$$c_{dissolved} = \kappa_H p_i$$
$$p_i V_{LFG} = nRT$$



Henry's Law Constant for PFAAs at 25 °C (Pa m^3 mol^{-1})
Source: Kwan (2001)

Assumptions

- PFAS in equilibrium with leachate
- Condensate accounted for with leachate
- PFAS leachate concentrations by Lang et al. (2017)

PFAS in LFG - Results

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PFAS	Molecular Weight (g/mol)	Henry Law Constant (Pa m^3 mol-1)	Concentration (ug/l)	Partial Pressure (atm)	Moles (-)	Mass (ug)
TFA	114.02	0.0121	1.0	8.16x10-7	0.16	0.02
PFPrA	164.03	0.1130	1.0	8.[illegible]x10-8	[illegible]	0.11
PFBA	212.08	1.2400	1.0	7.9[illegible]	0.06	0.01
PFPeA	264.05	1.5[illegible]00	1.0	6.58x10-9	0.05	0.01
PFHxA	314.0[illegible]	2.92[illegible]0	2.0	2.13x10-8	0.16	0.05
PFH[illegible]A	36[illegible].06	5730	0.8	1.38x10-8	0.10	0.04
[illegible]FOA	414.07	0.3620	1.0	2.73x10-8	0.21	0.09
TOTA[illegible]						1.01

NEGLIGIBLE

PFAS Input with Cover Materials

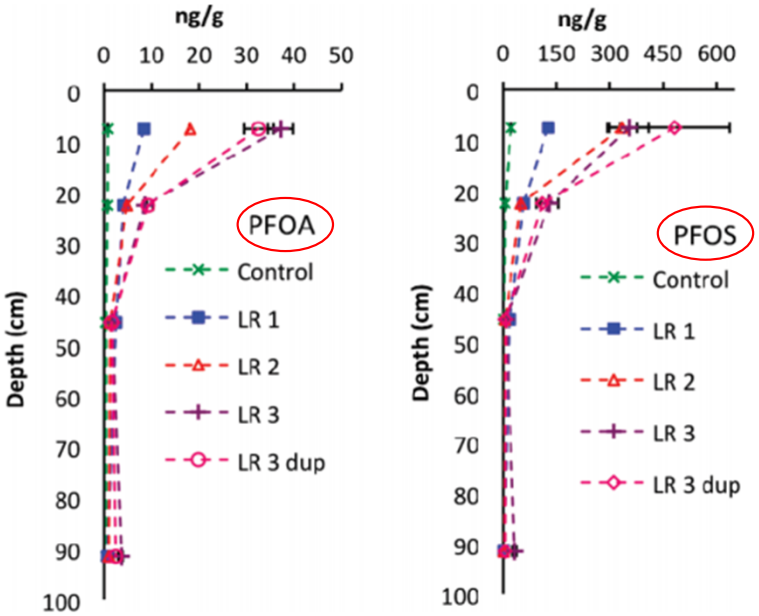
PFAS leaching from Soils (Source: McLachlan et al., 2019)

- PFAS leaching occurred within 49-120 days
- Soil/water partitioning $k_d \approx 0.5$
  - 50% mobile, i.e., leachable
  - 50% immobilized, i.e., retained in cover soil

Input with Cover Material

- Estimate cover as 20% of landfilled MSW
- 0.5% Biosolids in cover materials (Venkatesan and Halden, 2013)
- 50% of PFAS from cover materials is mobile
- PFAS in conventional Cover Soils: 10 ng/g

PFAS in Soils from Land Application of Biosolids



Source: Sepulvado et al. (2011)

Challenging Sampling and Analytical Matrix

Cover Materials PFAS Contribution

Component	Percentage	Result
Cover Materials	20% of landfilled MSW	2.54×10^{10} kg/yr
ΣPFAS from Cover Soils	99.5% @ 10 ng/g	252.7 kg/yr
ΣPFAS from Biosolids	0.5% @ 540 ng/g	68.6 kg /yr
Subtotal		321.3 kg/yr
Mobile ΣPFAS	50%	
ΣPFAS to Leachate from Cover Materials		**160.7 kg/yr**

ΣPFAS Mass Balance for MSW Landfills

Material	Inputs (kg/yr)	Outputs (kg/yr)
Landfilled Waste	12,257	
Landfilled Biosolids	527	
Cover Materials	161	
Precipitation	17	
Leachate		745
Precursors	745	
Landfill Gas		1
ΣPFAS, Subtotal	**13,707**	**1,491**
Net Change (kg/yr)	**12,216**	

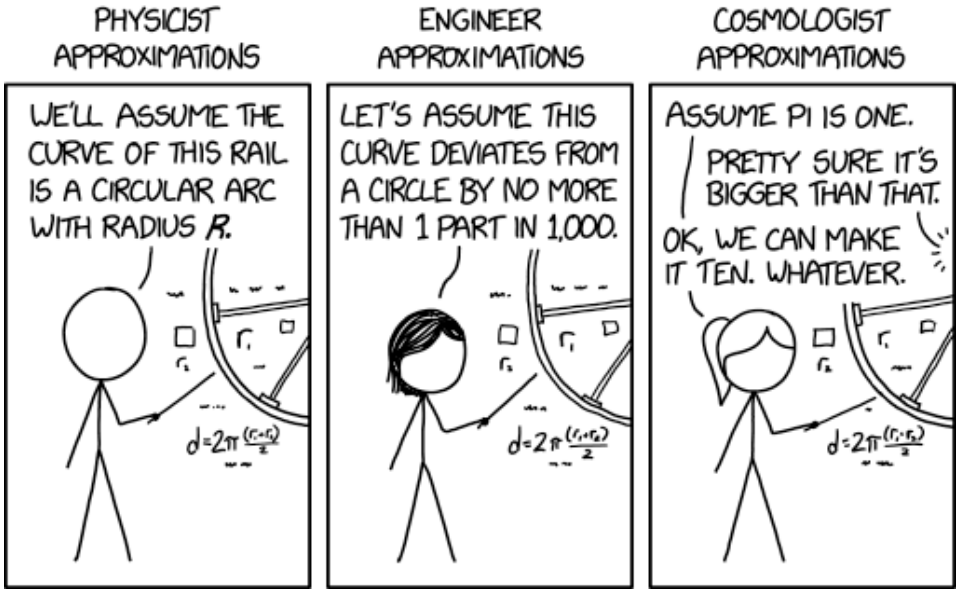
Approximately 10% of the landfilled PFAS Mass is released
Leachate is the predominant pathway for PFAS releases

Summary & Conclusions

On the national basis, landfills sequester PFAS

- Site-specific conditions may vary, dependent on local generators
- The largest inputs of PFAS are
  - Solid waste
  - Biosolids
  - Precursors
- LFG PFAS content and emissions - research on going
- Use of impacted cover soil –net neutral
- Biosolid land-application moratoria ➔ increased LF PFAS input
- Limited precursor conversion within landfills ➔ leachate/wastewater concern
- **Leachate is the predominant pathway for PFAS removal**

Questions? Comments?



Source: Russell Monroe (https://xkcd.com/2205/)

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