A SunCam online continuing education course

PFAS in Biosolids

by

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Course Outline:

PFAS Overview
PFAS Compounds
Biosolids Overview
PFAS Concentrations
Exposure Pathways
Federal Regulations
State Regulations
Lab Test Method
PFAS Removal, Destruction & Stabilization
Disposal Costs
Helpful References
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PFAS Overview

PFAS is an abbreviation for per- and poly-fluoroalkyl substances. PFAS are known as persistent organic pollutants or “forever chemicals” since they last for a very long time. PFAS production can be traced back to 1938 when a form of PFAS called PTFE was created in a DuPont lab. The water-resistant and heat-resistant properties made PFAS a popular choice for materials, coatings, and many consumer products. For example, PFAS was used for decades as a firefighting foam called AFFF (Aqueous Film Forming Foam). See Figure 1 for PFAS product examples.

Figure 1: Upper Left) PFAS coated fabric. Upper Right) PTFE lined pot.
Lower Left) Firefighting foam (AFFF). Lower Right) Popcorn bag with PFAS coating.

Source: Upper Left) wikimedia.org/wiki/File:A_water_droplet_DWR-coated_surface2_edit1.jpg, Brocken Inaglory, CC-BY-SA-3.0; Upper Right) wikimedia.org/wiki/File:Aluminium_steelpan_met_teflon_van_Van_Nelle,_objectnr_90815.JPG, Museum Rotterdam, CC-BY-SA-3.0; Lower Left) wikimedia.org/wiki/File:Autobrand_IJzendoorn.JPG, Fire Brigade Neder-Betuwe; Lower Right) wikimedia.org/wiki/File:Microwave-popcorn-showing-exponential-decay.jpg, Benjamin J. Burger, CC-BY-SA-4.0

Health Concerns

PFAS is linked to serious health problems in humans and other animals. Medical studies going back to the 1970's have shown direct links between many common types of PFAS chemicals and health problems. Figure 2 shows the main health impacts of excessive PFAS consumption.

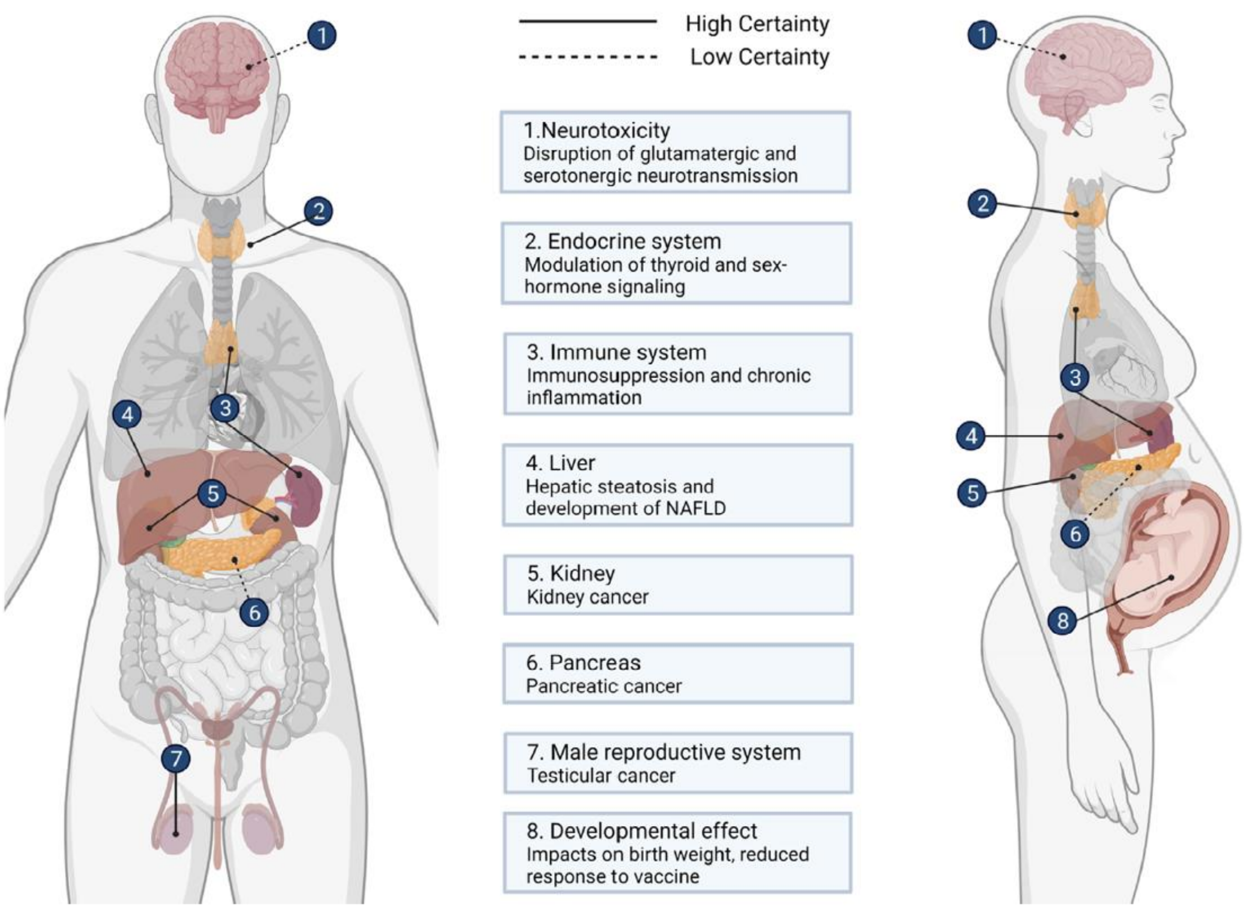


Figure 2: Health effects of PFAS in men (left) and women & fetuses (right).

Source: https://edition.pagesuite-professional.co.uk/html5/reader/production/default.aspx?pubname=&edid=f2856496-3b7f-4113-8461-af5d282d8066

PFAS can enter the human body through the consumption of food or liquid. PFAS molecules can be absorbed into the body and accumulate in human tissue, especially the liver and kidneys. Therefore, keeping drinking water and food products free of PFAS is important for human health.

Fate and Transport

PFAS begins its journey at a chemical manufacturing facility and then is distributed to various destinations, such as industrial, manufacturing, and military facilities. Many consumer products with PFAS end up in a landfill. Industrial waste streams with PFAS are either directly discharged to the environment or discharged to a publicly owned treatment works (POTW) with a wastewater treatment plant (WWTP) with a treated effluent going to the environment. See Figure 3.

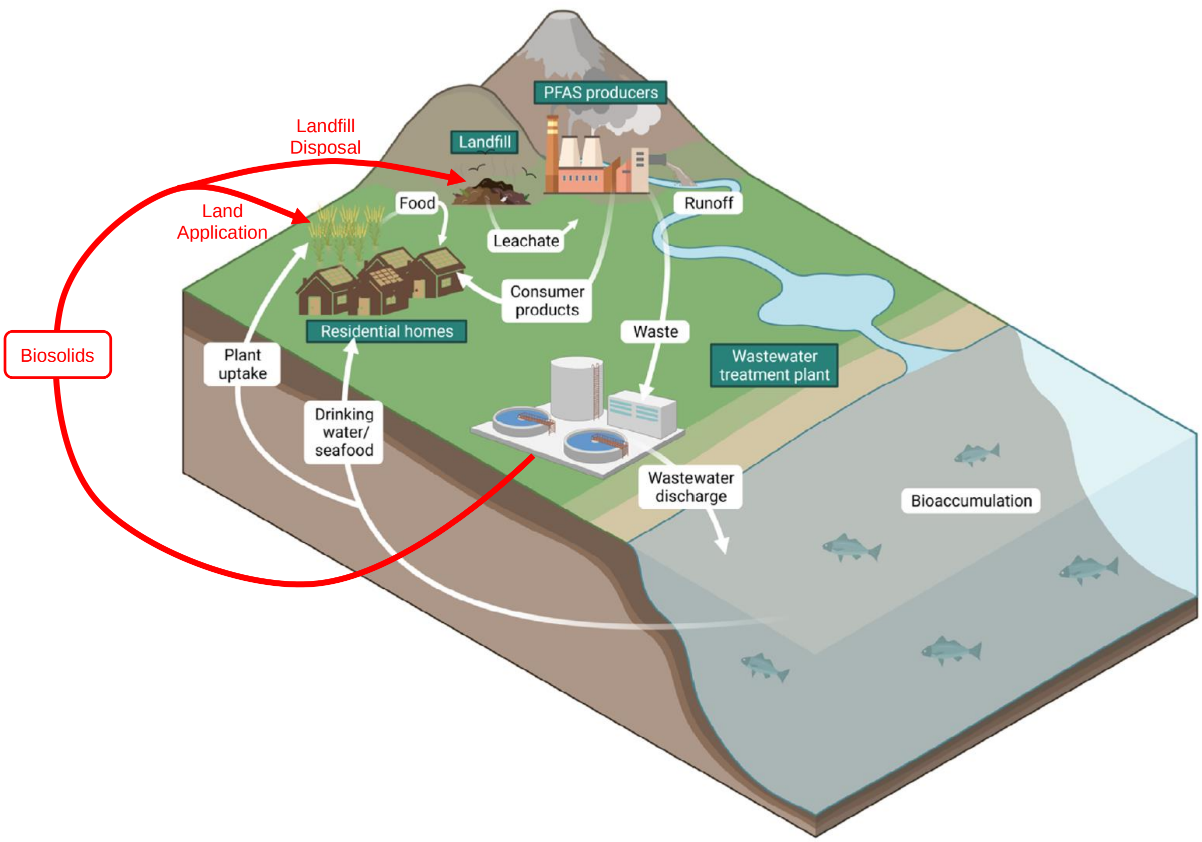


Figure 3: Environmental fate of PFAS with wastewater biosolids in red.
Source: https://edition.pagesuite-professional.co.uk/html5/reader/production/default.aspx?pubname=&edid=f2856496-3b7f-4113-8461-af5d282d8066, modified

Many WWTP processes produce sludge called biosolids which can have considerable amounts of PFAS. Biosolids are often land applied or disposed in a landfill. Land application can result in PFAS being absorbed in crops or accumulating in groundwater.

See the course entitled "PFAS in Drinking Water" for a history of PFAS impacts on the environment and water supplies.

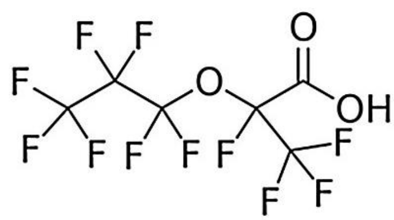
PFAS Compounds

There are thousands of different types (or compounds) of PFAS chemicals. The EPA toxicity database, DSSTox, lists 14,735 unique PFAS chemical compounds. All PFAS are made of a backbone of carbon atoms with each carbon bonded to two fluorine atoms. It is this row of carbon-fluoride bonds that makes the compounds last so long.

PFAS are classified according to these main differences:

1. If the chain (or backbone) of the compound has only carbon atoms (fully or per) or has non-carbon atoms (partly or poly). For example, the below PFAS, known as HFPO-DA or GenX, has an oxygen atom in the chain, so it is a poly PFAS.

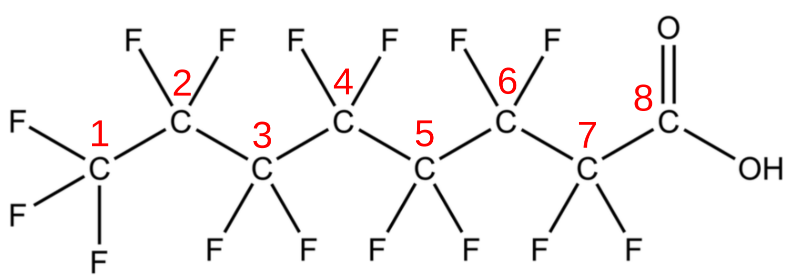
HFPO-DA or GenX:



2. Type of end ion (called the head):
   a. Perfluoroalkyl carboxylic acids (PFCAs), or carboxylates, have a $-CO_2$ ion.
   b. Perfluoroalkyl sulfonic acids (PFSAs), or sulfonates, have a $-SO_3$ ion.

3. Number of carbon atoms in the backbone (called the chain). For example, the below common PFAS called Perfluorooctanoic acid (PFOA) has 8 carbon atoms.

PFOA:



- Short-chains contain < 7 carbons for PFCAs and < 6 carbons for PFSAs.
- Long-chains contain ≥ 7 carbons for PFCAs and ≥ 6 carbons for PFSAs.
- Polymers contain ≥ 15 carbons for PFCAs and ≥ 14 carbons for PFSAs.

Note that Carboxylates have an extra carbon in the $-CO_2$ head, so the transitions to long-chain and polymer are one carbon atom higher.

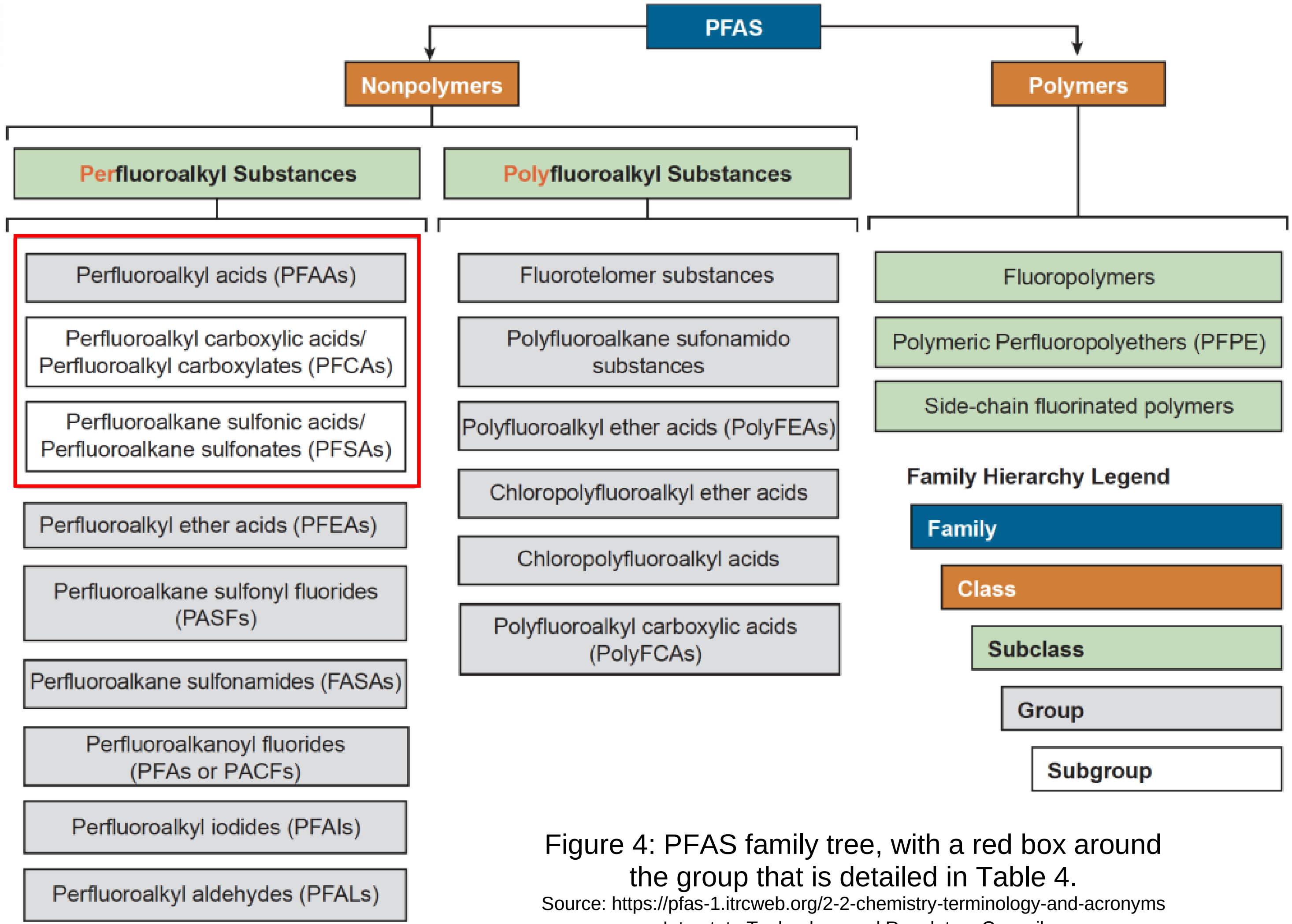
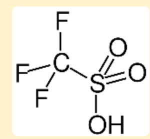
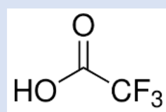
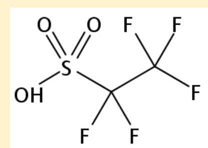
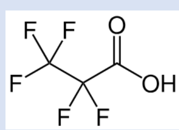
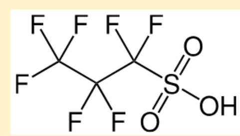
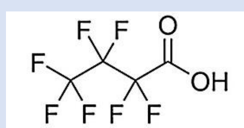
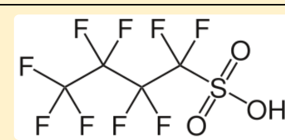
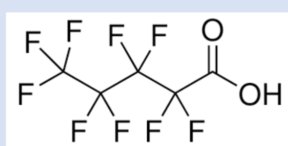
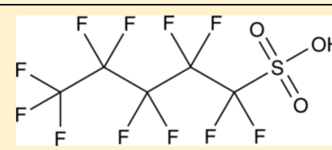
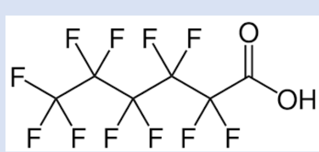
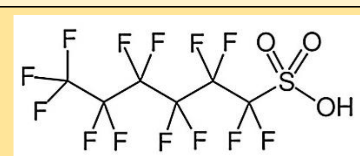


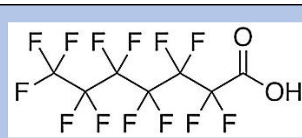
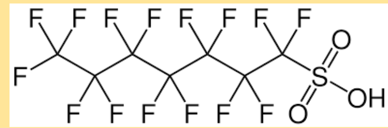
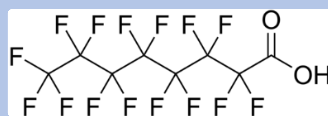
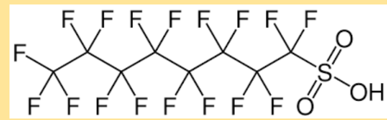
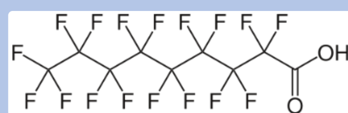
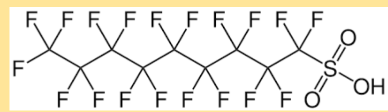
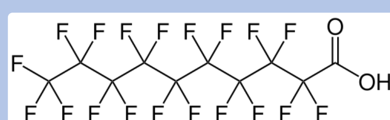
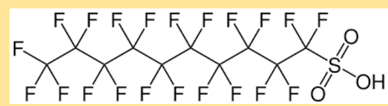
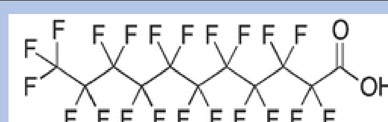
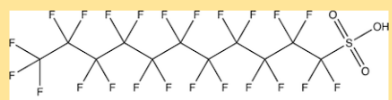
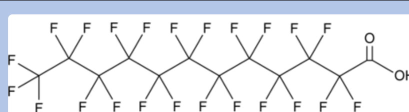
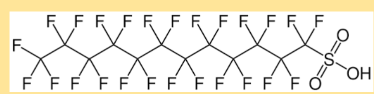
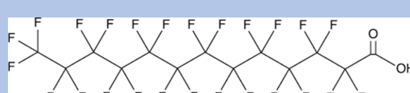
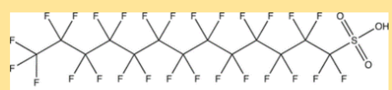
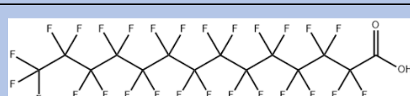
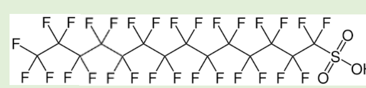
Figure 4: PFAS family tree, with a red box around the group that is detailed in Table 4.
Source: https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms
Interstate Technology and Regulatory Council

<u>Per PFAS Compounds</u>

Table 1 shows the short and long chain "Per-" PFAS compounds. Many of these PFAS must be tested for in water, wastewater, and biosolids. In the chemical diagrams are Lewis Structures with carbon atoms at junctions without a letter, as is customary.

Table 1: "Per-" PFAS Compounds by Chain Length and Head Type

No. of Carbons	Carboxylates (PFCAs)		Sulfonates (PFSAs)	
1	Short-chain	None	Short-chain	 **TFMS**
2		 **TFA**		 **PFEtS**
3		 **PFPrA**		 **PFPrS**
4		 **PFBA**		 **PFBS**
5		 **PFPeA**		 **PFPeS**
6		 **PFHxA**	Long-chain	 **PFHxS**

7		 **PFHpA**		 **PFHpS**
8		 **PFOA**		 **PFOS**
9		 **PFNA**	Long-chain	 **PFNS**
10	Long-chain	 **PFDA**		 **PFDS**
11		 **PFUnA**		 **PFUnS**
12		 **PFDoA**		 **PFDoS**
13		 **PFTrDA**		 **PFTrDS**
14		 **PFTeDA**	Poly-mer	 **PFTeDS**
15+	Poly-mer	Various		Various

Biosolids Overview

Biosolids are solid organic matter that is a byproduct of wastewater treatment processes. Biosolids are also known as residuals, sewage sludge, biosludge, dewatered sludge, or dried sludge. Biosolids are produced at nearly every municipal WWTP. Industrial WWTPs with biological processes produce sludge which is sometimes considered biosolids.

There are a variety of treatment processes that can produce sludge, resulting in a variety of different types of sludge, as shown in Table 2. Dewatered or dried sludge can be considered biosolids.

Table 2: Sludge Types and Land Application Potential

Sludge Type	Treatment Processes	Percent Solids	Potential for Land Application
Screenings	Basket, Bar Screen, Perforated Plate, Compactor, Sieving	10 to 30	Very Low
Grit	Classifier, Collector, Vortex, Centrifugal, Grit Chamber, Detritus Tank, Chain & Bucket	3 to 6	Very Low
Scum	Scum Trough, Oil-Water Separator, Grease Interceptor	0.1 to 2	Very Low
Raw	Preliminary, EQ Tank Solids, Oil-Water Separator, Grease Interceptor	3 to 7	Low
Primary	Sedimentation, Chemical Precipitation, DAF, Grit Removal	3 to 5	Low
Secondary	Biological, MBR Activated Sludge	0.5 to 4	Medium
Tertiary	Sedimentation, Ion Exchange, Chemical Precipitation, Filtration, Lagoon Dredging	1 to 8	Medium High
Digested	Aerobic, Anaerobic Digestion Upflow filter, Fluidized bed, UASB	3 to 12	High
Thickened/ Dewatered	Screw Press, Centrifuge, Belt Press, Gravity Thickener	10 to 25	Very High
Dried	Drying Bed, Reed Bed, Heating, Evaporation, Plate and Frame Filter Press	65 to 90	Very High

Screenings, grit, and scum are typically disposed directly to a waste management facility such as a landfill. Sometimes raw sludge is also. The various other sludges from treatment processes are normally combined and digested, thickened, dewatered, and/or dried to reduce the volume of liquid to handle and transport. See Figure 5 for a block flow diagram of a conventional wastewater treatment plant in which sludge flows are combined, thickened, and digested prior to disposal.

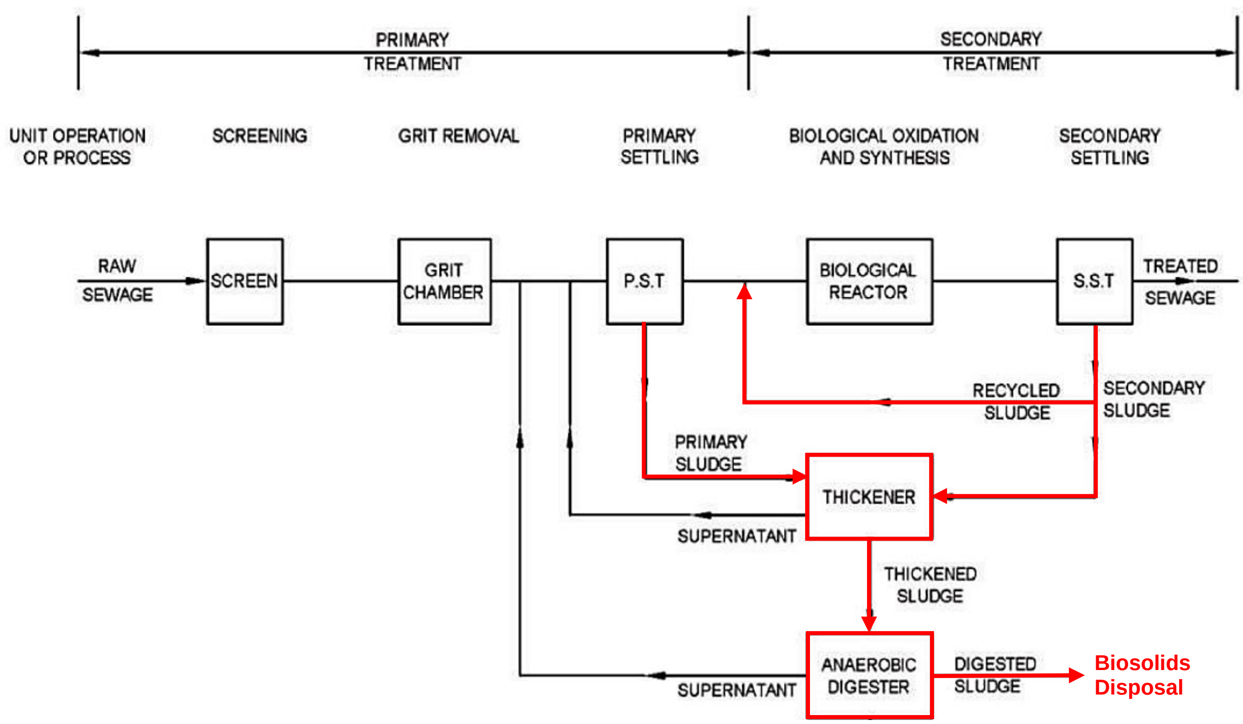


Figure 5: Traditional WWTP processes with sludge flows in red.

Source: "Manual on Sewerage and Sewage Treatment" 2nd Ed, by India Ministry of Urban Development (public domain)

Figure 6 shows a common method for testing the quality of primary and secondary sludge. These tests help engineers and operators adjust treatment system parameters to optimize wastewater treatment and produce good quality sludge.

Figure 6: Testing the settleability of sludge in wastewater with the sludge volume index (SVI) method. Good quality sludge has an SVI range of 50 to 150 mL/gram.
Source: wikimedia.org/wiki/File:Sludge_volume_index_test_(28227277273).jpg, SuSanA Secretariat, CC-BY-2.0

Secondary biological sludge is called activated sludge as it contains active/living organisms as shown in Figure 7. Digesting this sludge helps to “stabilize” the sludge, which makes it easier to dewater and reduces odors. The resulting low water content sludge (similar to Figure 8) is then ready for trucking offsite for disposal.

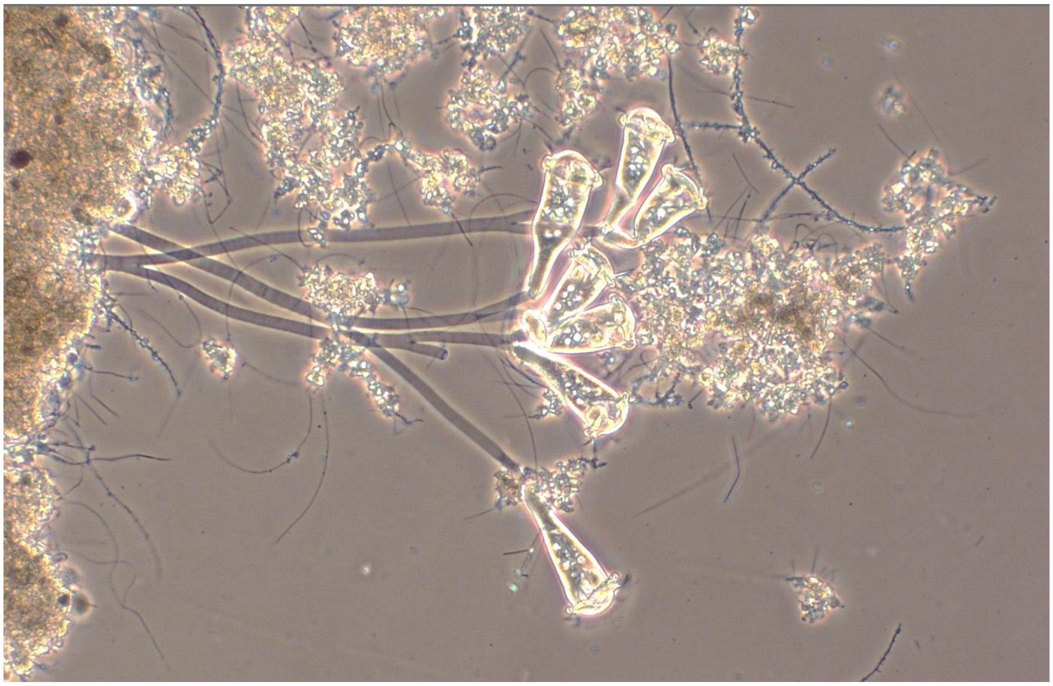


Figure 7: Biological “activated” sludge with stalked ciliates.
Source: www.epa.gov/sites/default/files/2021-06/documents/microbiologypresentation.pdf, public domain

Figure 8: Sludge being dried by evaporation in a sludge drying bed.
Source: wikimedia.org/wiki/File:Lit_de_s%C3%A9chage_des_boues_-_sludge_drying_bed_(Morrocco)_(9717585791).jpg, Morrocco, CC-BY-2.0

Disposal of Biosolids

Biosolids can be disposed of in several different ways, as depicted in Figure 9. The most popular options are land application, incineration, and landfilling. Of these, land application has the greatest potential for PFAS being introduced into the environment.

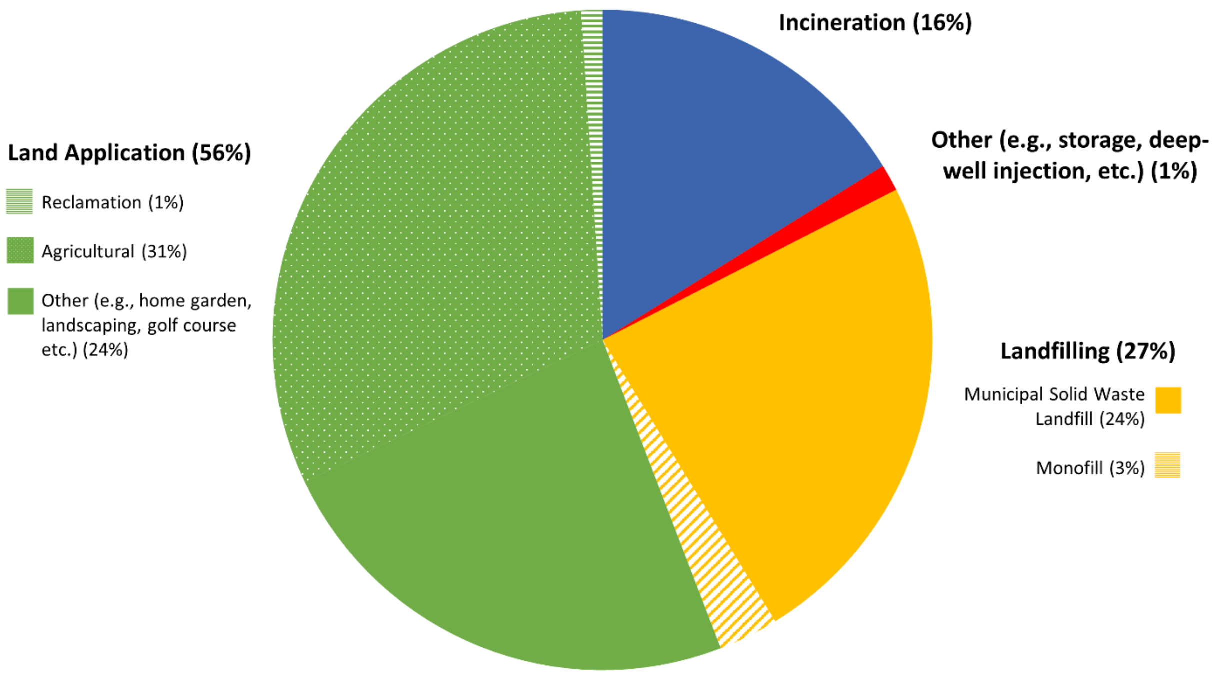


Figure 9: Biosolids disposal destinations for U.S. municipal WWTPs in 2022.
Source: www.epa.gov/system/files/images/2023-12/2022-bars-use-disposal-data-12.14.23.png, public domain

When applied to land, biosolids provide several benefits including nutrient addition, reduced fertilizer demand, improved soil structure, reduced irrigation requirements, and conservation of landfill space. The following are descriptions of land application options.

Reclamation

Restoring degraded land to make it productive is called land reclamation. Examples include industrial sites, brownfields, mines, quarries, landfills, and paved areas. Biosolids can be applied to revive the soil and create an open space, public park, wildlife habitat, agriculture field, residential homes, or commercial development. Soil regeneration is essential for reclaiming sites with little or no topsoil. Biosolids are proven to quickly establish a healthy soil base.

Agricultural

Land application for agriculture is the most popular disposal method for biosolids. The goal is to provide a healthy soil structure and to provide nutrients for crops to grow. The biosolids should be applied to land at the “agronomic rate,” which is the application rate (dry weight of solids applied per acre) that provides just enough nutrients for crop growth. The three main nutrients are nitrogen (N), phosphorus (P) and potassium (K), together known as NPK.

The agronomic rate is dependent on crop type, geographic location, and soil characteristics. Testing of the sludge and soil helps determine the agronomic rate. Loading rates of pollutants also need to be kept below regulatory limits which can restrict the sludge application rate. And biosolids should not be applied when the ground is frozen. Thus, in many cases a combination of biosolids and fertilizer is utilized to achieve ideal nutrient levels in the soil.

Figure 10: Liquid biosolids being spread on a farm field between rows of crops.
Source: wikimedia.org/wiki/File:Application_of_liquid_sludge_(6305085999).jpg, SuSanA Secretariat, CC-BY-2.0

Home Garden

Biosolids can be processed and packaged for commercial sale as bags of fertilizer. Your local hardware store or garden center may have bags of biosolids for sale, such as those shown in Figure 11. The fertilizer can be added to the garden, lawn, and potted plants to promote plant growth.

Figure 11: Example wastewater biosolid products for sale as fertilizers.
Source: www.mmsd.com/about-us/milorganite, www.dcwater.com/biosolids, mwrd.org/what-we-do/biosolids

Landscaping and Grass

Biosolids are often added as a fertilizer and soil enhancer for turfgrass, athletic fields, golf courses, sod, lawns, rangelands, and landscaping.

Composting

Biosolids can be mixed with biomass, such as wood chips and food scraps, to create a compost mixture. Compost has many uses including the following:

- Garden soil enhancer
- Flower bed soil
- Potting soil
- Incorporating into tree beds
- Feeding fall perennials
- Feeding spring bulbs

Forestry

Biosolids are proven to enhance timber growth. Applying biosolids around trees makes the trees grow faster and stronger, which can help a forest recover after tree removal. Biosolids are also used to grow trees meant for harvesting.

Classes of Biosolids

Biosolids that are land applied must meet federal and state requirements. This involves classifying the biosolids as Class A-EQ, A, B, or Unclassified, based on pollutant and pathogen limits, as defined in Title 40 of the Code of Federal Regulations (CFR) Chapter 503.13 (40 CFR 503.13). Table 3 shows the CFR codes that define the biosolids classification.

Table 3: Biosolids Classification Requirements

	Pollutant Limit Requirement § 503.13 (a)(1)-(a)(4) and § 503.13 (b)(1)-(b)(4)		**Pathogen Requirements § 503.15(a) § 503.32 (a)(3)-(a)(8) and § 503.32 (b)(2)-(b)(4)**	**Vector Attraction Reduction Requirement § 503.15(c) § 503.33 (b)(1)-(b)(10)**
Class A Exceptional Quality (EQ)	Ceiling Concentrations (a)(1)	Pollutant Concentration (b)(3)	Any Class A Alternative (a)(3)-(a)(8)	Any Alternative 1-8 (b)(1)-(b)(8)
Class A	Ceiling Concentrations (a)(1)	Pollutant Concentration (a)(2)-(a)(4) or (b)(3)	Any Class A Alternative (a)(3)-(a)(8)	Alternative 9 or 10 (b)(9) or (b)(10)
		Cumulative Pollutant Loading Rates (a)(2) or (b)(2)		Any Alternative 1-10 (b)(1)-(b)(10)
		Annual Pollutant Loading Rates (a)(4) or (b)(4)		Any Alternative 1-8 (b)(1)-(b)(8)
Class B	Ceiling Concentrations (a)(1)	Pollutant Concentration (a)(2)-(a)(4) or (b)(3)	Any Class B Alternative (b)(2)-(b)(4)	Any Alternative 1-10 (b)(1)-(b)(10)
		Cumulative Pollutant Loading Rates (a)(2) or (b)(2)		Any Alternative 1-10 (b)(1)-(b)(10)

Table 4 shows concentration limits required to be Class A-EQ, A or B biosolids. There are similar tables for loading rates and pathogen removal requirements.

Table 4: Biosolids Pollutant Concentration Limits

Concentration Limits		
Pollutant	**Ceiling Concentrations (Table 1 of 40 *CFR* 503.13) (milligrams per kilogram, dry weight)**	**Pollutant Concentrations (Table 3 of 40 *CFR* 503.13) Monthly Average (milligrams per kilogram, dry weight)**
Arsenic	75	41
Cadmium	85	39
Chromium	3,000	1,200
Copper	4,300	1,500
Lead	840	300
Mercury	57	17
Molybdenum*	75	--
Nickel	420	420
Selenium	100	36
Zinc	7,500	2,800

Land Use by Class

- Class A-EQ is the best quality biosolids and generally allowed for any land application, home gardens, or other public uses. In some states such as Florida, this class is known as Class AA biosolids with state specific requirements.
- Class A biosolids can be land applied with little to no crop harvesting restrictions although buffer zones are required between sludge application and adjacent properties.
- Class B biosolids can be used for commercial row crops (with limited application rates), field crops, feed crops, pasture, and hay land agriculture.
- Unclassified sludge is typically not allowed to be land applied.

Pollutants in Biosolids

PFAS is just one of hundreds of pollutants that can be present in biosolids. As part of the initial classification process, wastewater sources (industrial, domestic, landfill leachate, etc.) are analyzed and sludge testing performed to identify potential pollutants. The presence of a pollutant alone does not mean that the biosolids pose harm to human health or the environment. The concentration and application rate are important considerations to assess the potential harm of pollutants.

PFAS Concentrations

Pollutant concentrations in biosolids can be measured as:

- Dry weight (ng/g dry) (mg/kg dry) (µg/kg dry)
- Wet weight (ng/g wet) (mg/kg wet) (µg/kg wet)
- Wet volume (mg/L) (µg/L) (ng/L).

Dry weight is the conventional unit since it is more convenient for loading rate calculations and dry weight is used in 40 CFR 503. With biosolids, parts per trillion (ppt) is ng/kg or ng/L and parts per billion (ppb) is ng/g or µg/L. See Tables 5 and 6 for actual weight-based PFAS concentrations in biosolids.

Wet volume concentration can be converted to wet weight by using the biosolids/sludge density (ρ), which is normally 1.0 to 1.3 kg/L (s.g. 1.0 to 1.3).

$$\text{A mg/kg wet} = \frac{\text{B mg/L}}{\rho \text{ kg/L}}$$

Wet volume concentration can be converted to dry weight by using the percent solids and the below "wet to dry formula". This formula is approved by the EPA, although at high percent solids it is less accurate due to the density difference with water. See Table 2 for typical percent solids values

$$\frac{\text{A mg/L(wet)}}{\text{\% Total Solids}} = \text{B mg/kg(dry)}$$

$$\text{where } \text{\% Total Solids} = \frac{\text{weight of sample dry}}{\text{weight of sample wet}} \text{ x } 100$$

Wet volume can be converted to daily dry weight with the following "pounds formula", assuming the sludge/biosolids density is similar to water:

Load (lb/d) = Conc. (mg/L) * Flow (MGD) * 8.34

Table 5: Measured Concentrations of PFOA and PFOS in U.S. Municipal Biosolids

Year Sampled	PFOA (ng/g dry wt)	PFOS (ng/g dry wt)	Reference
2001	12 - 70	308 - 618	Venkatesan, 2013
2004-2007	8 - 68	80 - 219	Sepulvado, 2011
2005	16 - 219	8.2 - 110	Loganathan 2007
2005	18 - 241	<10 - 65	Sinclair, 2006
2006	--	81 - 160	Schultz, 2006
2006-2007	18 - 69	31 - 702	Yu, 2009
2007	20 -128	32 - 418	Yoo, 2009
2011	1 - 14	4 - 84	Navarro, 2016
2014	10 - 60	30 - 102	Mills, Dasu (in prep)
2018	1-11	2 – 1,100	EGLE, 2020

Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

Table 6: Measured PFAS Concentrations (ng/g) in Various Biosolids around the World

Country	Number of studies	Total number of plants surveyed	PFHxS	PFOS	PFHxA	PFOA
China and Hong Kong	7	148	0.15 – 59.42	3 – 1191	23	3.75 – 1517
US	9	136	<10 – 5.90	22 – 403	6.2 – 7.7	11 – 107
Germany	4	1,172	ND – 1.2	3.4 - 100	ND - 1	0.3 – 14
Greece	2	3	ND – 2.6	4.3 – 32	ND – 4.3	2.7 – 157
Spain	3	33	ND – 0.08	1.7 – 229	1.33 – 11	0.3 – 21
Czech Republic	1	43	NA	963	NA	NA
Other Asia*	4	40	6 – 97	14 - 474	50	11 – 73
Switzerland	2	71	1.5 – 240	5 - 158	0.8 - 3	0.9 – 7.2
Africa	2	19	0.03 – 0.25	0.2 – 0.4	0.2	0.09 – 0.17
Canada	1	6	NA	104	NA	1.64
Nordic Countries	3	24	0.01 – 3.6	0.13 - 18	0.13 – 1.15	0.2 – 1
Australia	2	25	0.7 – 2	22 - 67	2.6 - 2.8	8 – 11

*South Korea, Singapore and Thailand

Source: www.awa.asn.au/resources/latest-news/community/public-health/pfas-in-biosolids-a-review-of-international-regulations

<u>Example Problem 1</u>

The Acme WWTP receives an influent flow of 1 MGD with a PFOS concentration of 20 ppt (ng/L). On average, 90 percent of the PFOS goes into the sludge which is dewatered into biosolids with 20 percent solids and daily volume of 500 gal/d. What is the PFOS load (g/d) and concentration (ng/g dry) in the biosolids?

Solution:
First, calculate the PFOS load in the influent:

Influent PFOS (g/d) = 20 ng/L * 1E6 gal/d * 3.785 L/gal * 1 g/1E9 ng = 0.076 g/d

Then, multiply by 90% for the PFOS load to sludge and biosolids:

Biosolids PFOS (g/d) = 0.076 g/d * 0.9 = **0.068 g/d**

Next, use the daily volume-based PFAS concentration:

PFAS conc. = 0.068 g/d / (500 gal/d * 3.785 L/gal) * 1000 mg/g = 0.036 mg/L

Now, use the “wet to dry formula” and % solids to convert to dry concentration:

PFAS conc. (mg/kg dry) = 0.036 mg/L / 0.20 = 0.18 mg/kg dry

Finally, convert to ng/g dry:

PFAS conc. = 0.18 mg/kg dry * 1E6 ng/mg * 1 kg/1000g = **180 ng/g dry**

Exposure Pathways

Pollutants in biosolids can be transferred to humans or the environment through various pathways. Understanding these pathways can help prevent exposure and determine acceptable pollutant limits. Possible fate and transport pathways are identified and calculations performed in what are called conceptual models, exposure pathway models, or fate and transport models. These models are very similar for PFAS as for other pollutants.

Key conceptual models for the three main biosolids disposal methods are as follows:

1. Land Application -> Human Exposure
2. Land Application -> Ecological Exposure
3. Incineration -> Human Exposure
4. Incineration -> Ecological Exposure
5. Landfill (Surface) Disposal -> Human Exposure

See Figures 12 to 16 for example transport block diagrams for each of the above. The goal is to restrict the biosolid PFAS loads such that human and wildlife exposure is below the toxicity thresholds (term used for wildlife) and exposure limits (term used for humans). Ongoing medical studies, the Centers for Disease Control and Prevention (CDC), and the Food and Drug Administration (FDA) continue to refine estimated exposure limits for various PFAS substances for different population groups.

A common pathway is from biosolids to groundwater to drinking water to humans. In 2022, the USEPA published the following health advisory levels for the regular consumption of drinking water, where ppt is parts per trillion (ng/L):

- 0.004 ppt for PFOA (proposed limit of 4 ppt),
- 0.02 ppt for PFOS (proposed limit of 4 ppt),
- 10 ppt for HFPO-DA (GenX), and
- 2000 ppt for PFBS.

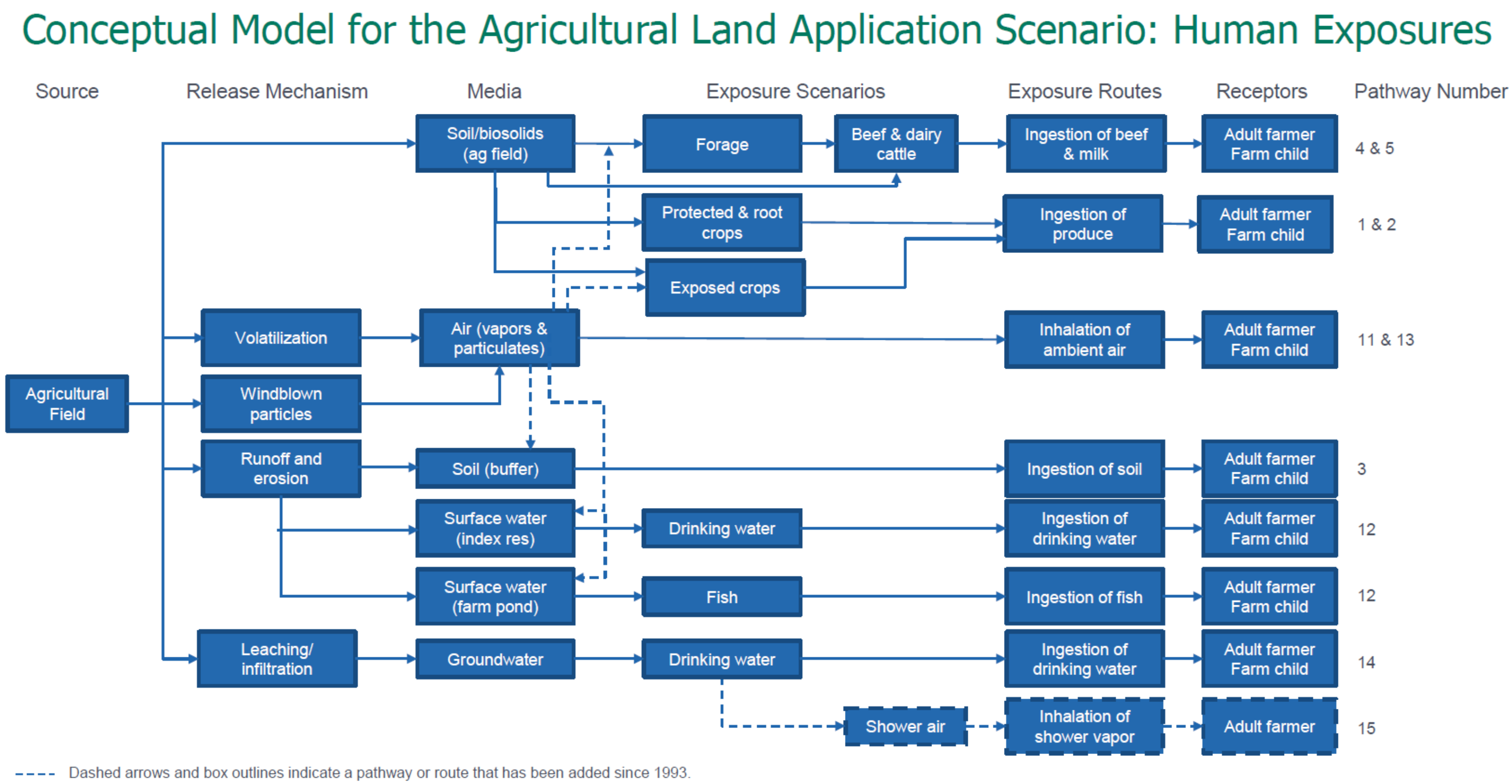


Figure 12: Transport block diagram for human exposure to pollutants in biosolids via land application.
Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

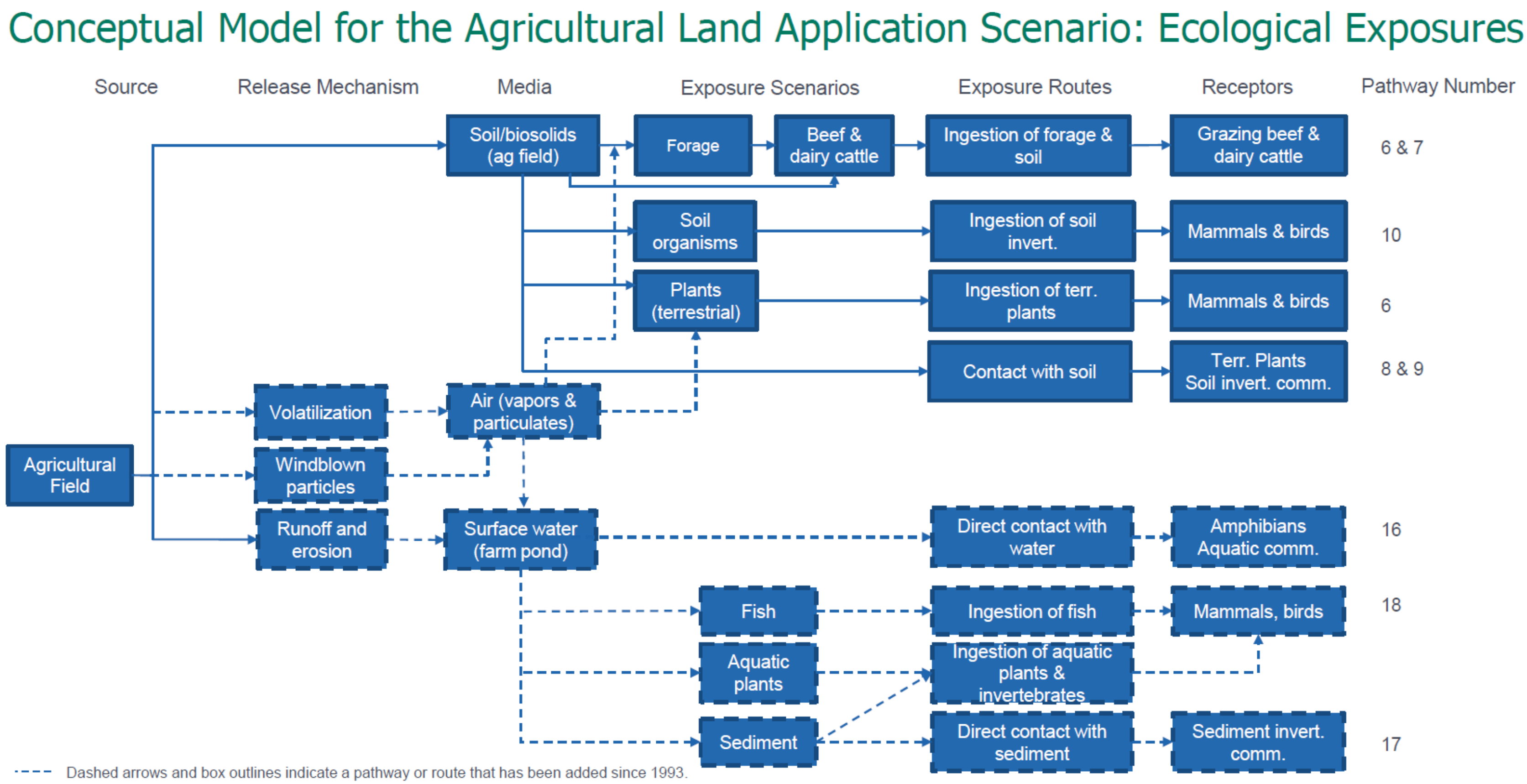


Figure 13: Transport block diagram for ecological exposure to pollutants in biosolids via land application.
Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

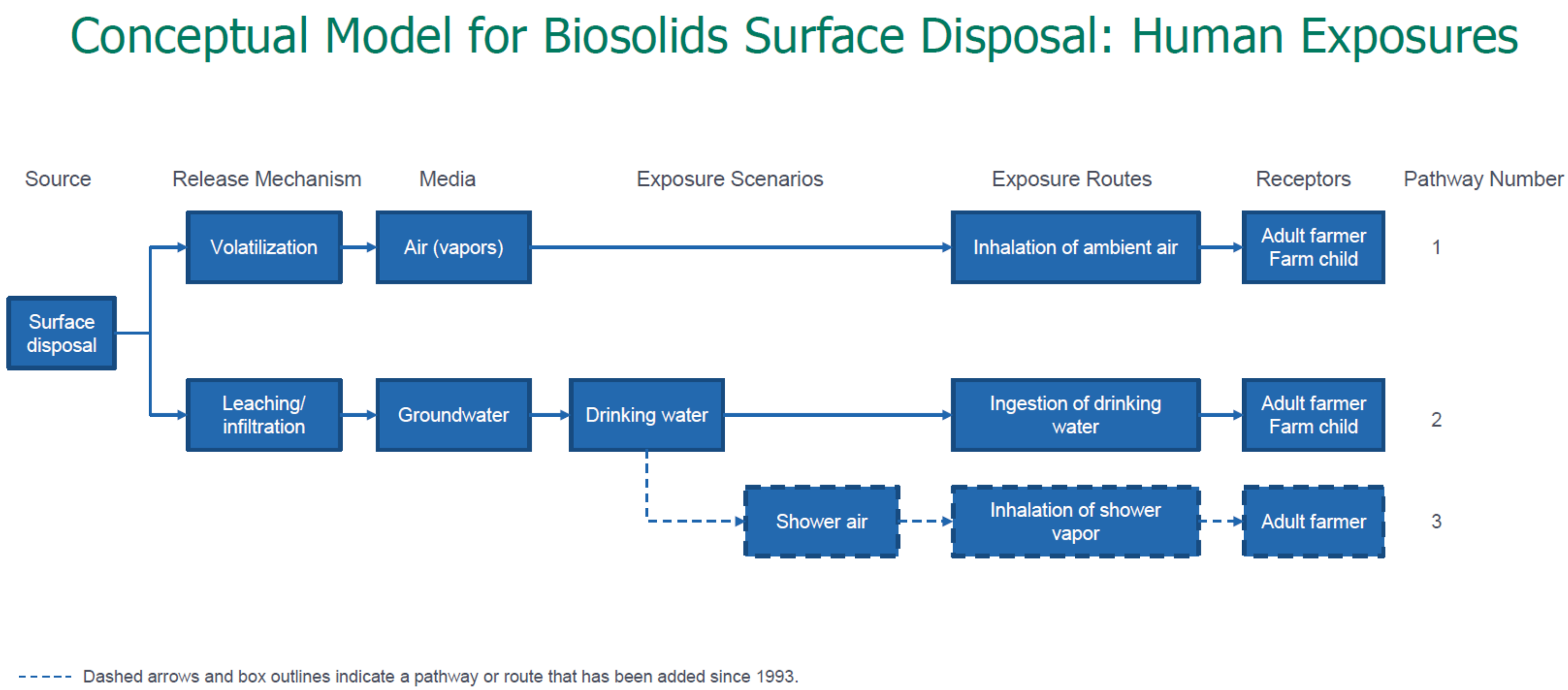


Figure 14: Transport block diagram for human exposure to pollutants in biosolids via landfill disposal.
Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

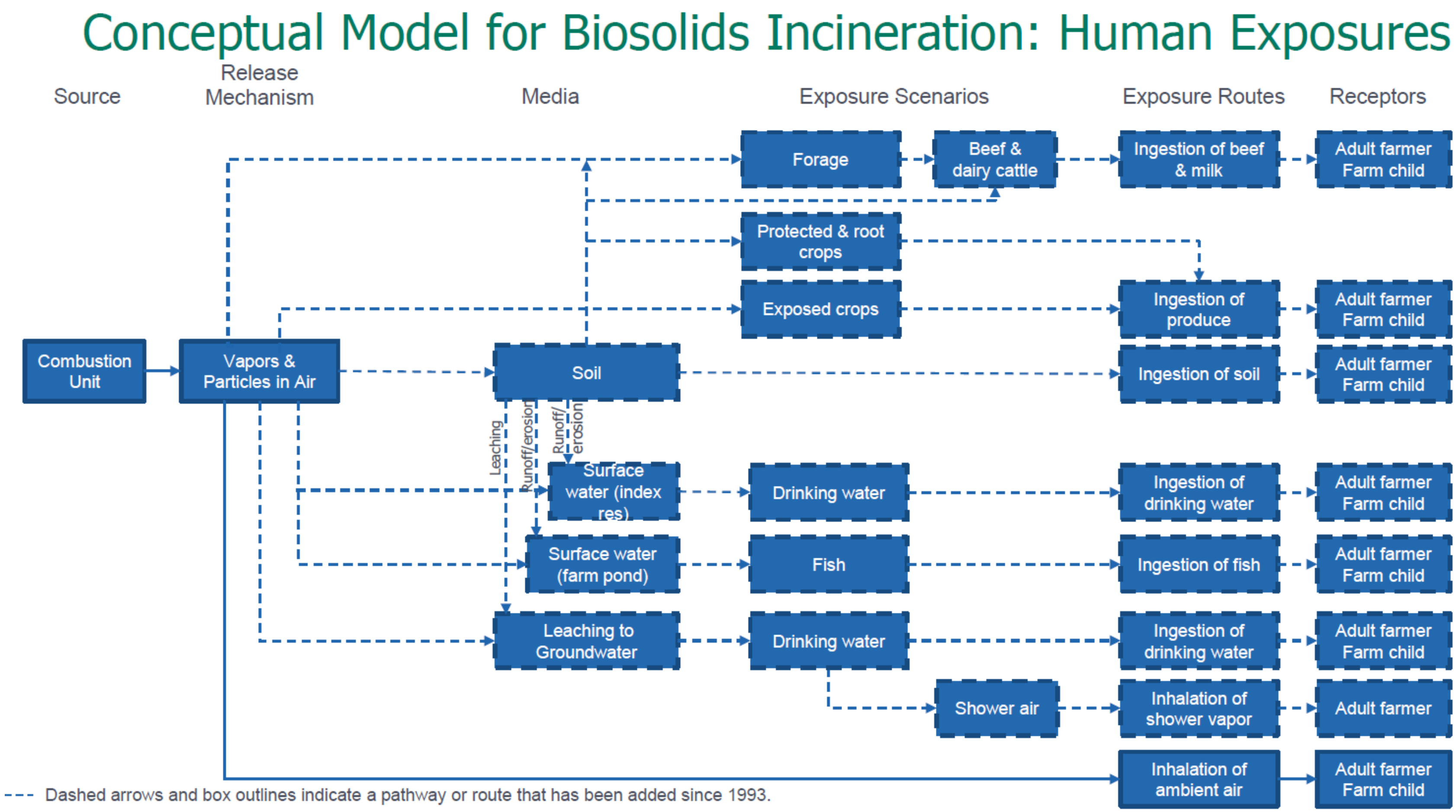


Figure 15: Transport block diagram for human exposure to pollutants in biosolids via incineration.
Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

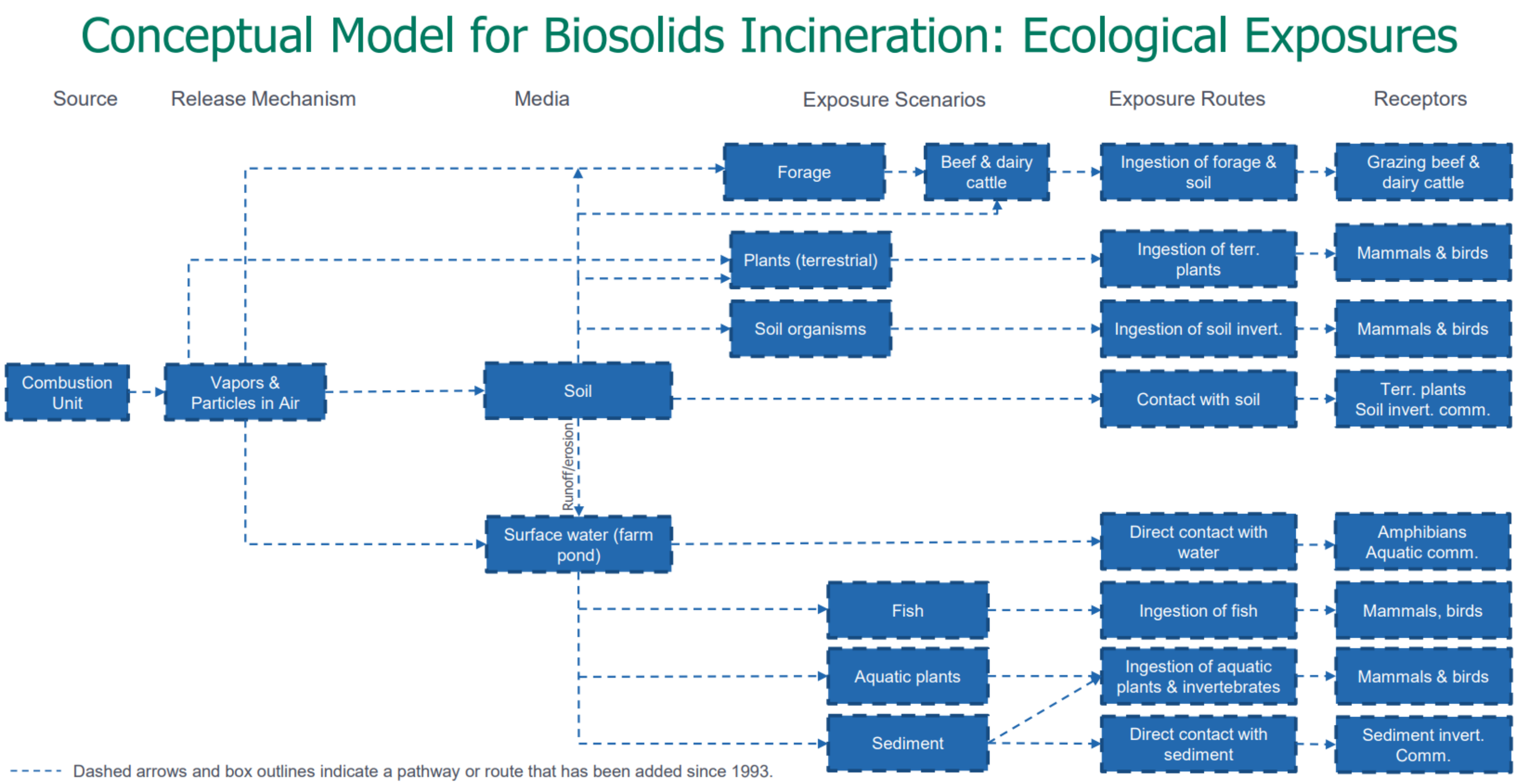
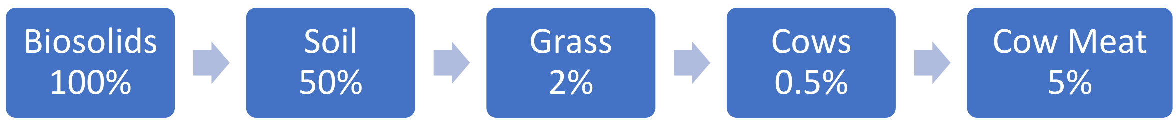


Figure 16: Transport block diagram for ecological exposure to pollutants in biosolids via incineration.
Source: www.epa.gov/sites/default/files/2021-02/documents/biosolids-pfoa-pfos-meeting-summary-nov-2020.pdf

Example Problem 2

Continuing Problem 1, the Acme WWTP has offered Acme Farms 200 gal/d of biosolids which can be land applied as a fertilizer to a pasture field for cow grazing. The biosolids PFOS concentration is 180 ng/g dry and 20 percent solids. Below is a transport block diagram with estimated percent of PFOS passed to each process. The farm harvests an average of 100 kg/d wet of cow meat (cuts and ground beef). What is the anticipated PFOS concentration (ng/g wet) in the meat?



Solution

Since biosolids is in volume, use the "wet to dry formula" to convert from dry to wet:

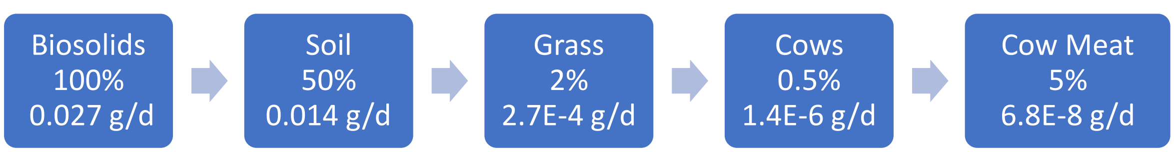
PFOS mg/L = mg/kg dry * % solids

= (180 ng/g * 1mg/1E6 ng * 1000g/1kg) * 0.20 = 0.036 mg/L

Next, calculate the daily PFOS load by multiplying the PFOS concentration by the biosolids volume per day and converting to g/d:

PFOS (g/d) = 0.036 mg/L * 200 gal/d * 3.785 L/gal * 1g/1000mg = 0.027 g/d

The load of PFOS reduces as it "transports" through each process according to the percentages in the block diagram. To obtain loads by process, multiply the load (g/d) from the previous process by the percentage going to the next process:



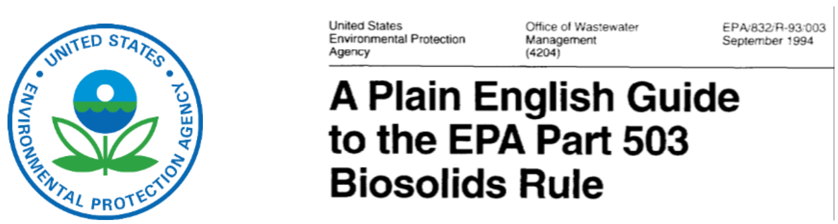
The PFOS concentration in the meat can be estimated with the concentration formula:

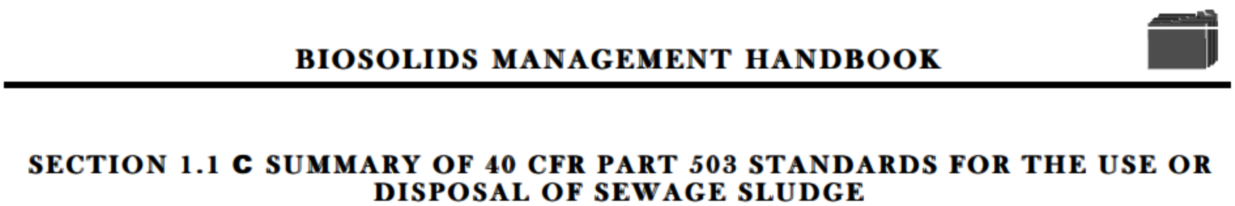
= 6.8E-8 g/d / 100 kg/d wet meat * 1E9 ng/g * 1kg/1000g = **6.8E-4 ng/g wet**

This example is to portray the transport of a PFAS compound through the environment due to biosolids disposal. The actual percentages passing through each process would be different in a real application.

Federal Regulations

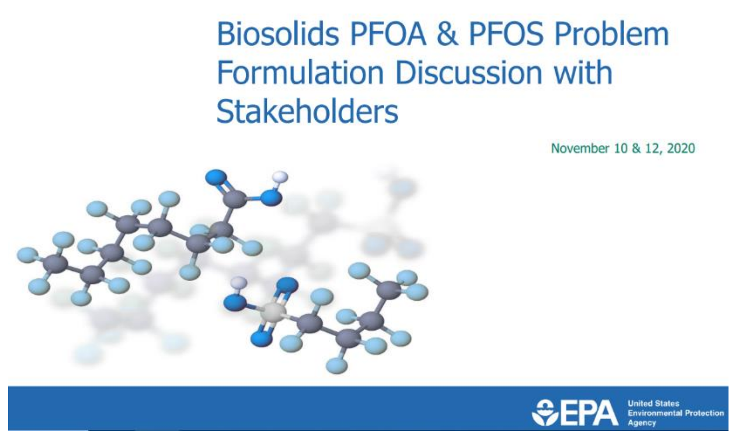
Biosolids that are land applied in the United States must meet requirements defined in Title 40 of the Code of Federal Regulations (CFR) Part 503 entitled “Standards for the Use or Disposal of Sewage Sludge”. This includes classifying the biosolids as Class A-EQ, A, or B, based on pollutant and pathogen limits. However, 40 CFR 503 does not include criteria for PFAS. The USEPA has released several documents to help apply the requirements in 40 CFR 503, including these two:





The USEPA is in the process of conducting a risk-based assessment of PFAS in biosolids, which is expected to result in testing requirements and limits for common PFAS compounds. USEPA will complete the risk assessment by the end of 2024 for the two most common compounds, PFOA and PFOS.

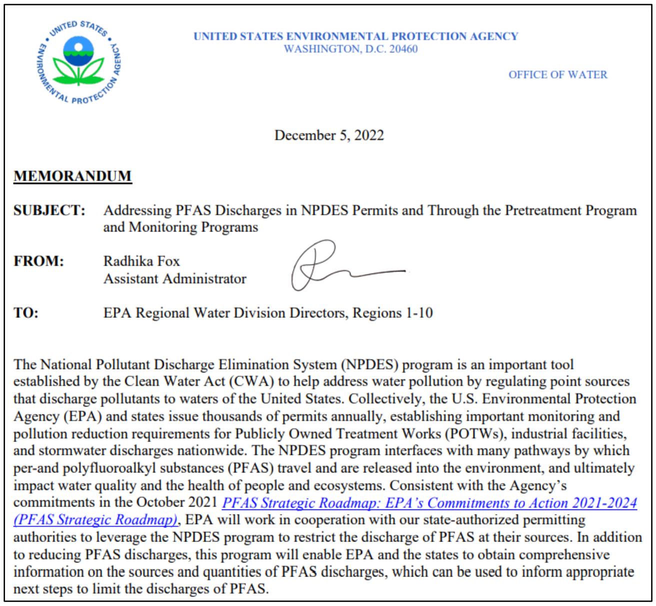
In November 2020, the USEPA held a meeting called “Biosolids PFOA & PFOS Problem Formulation”. On the right is the first slide from the meeting presentation:



The following are key notes from the USEPA 2020 meeting:

- PFAS sources of concern include paper mills and residuals, industrial cleaning products, floor wax (e.g., in schools), metal coating facilities, consumer products (e.g., textiles), car washes, and aqueous film forming foam. Some sources of concern cannot be discussed due to ongoing litigation at the state level.
- Since PFAS are ubiquitous in the environment, the conceptual models should account for background levels of PFAS in soil, surface water, and ground water. PFAS may be present on land application sites due to pesticide applications.
- NHDES and USGS are conducting a PFAS soil leaching study to calculate soil partition coefficients.
- If EPA determines that PFOA or PFOS in biosolids may adversely affect public health or the environment, risk managers will consider options for numerical limitations and best management practices for these compounds. Any subsequent proposed regulation would go through a standard rulemaking process including intra-Agency and Office of Management and Budget review.
- Biosolids risk assessment and regulation for PFAS should have a high-level strategy that includes pretreatment and manufacturing. Source control rather than continuous removal of chemicals from biosolids is key.
- Wastewater treatment plant infrastructure improvements to remove PFAS from sludge and biosolids requires large economic investments.
- Consider the big picture to protect the quality of biosolids for beneficial use. Any moratorium on land application is not sustainable for the industry.
- All three use and disposal practices for biosolids (land application for beneficial use, surface disposal, and incineration) are critical for successful biosolids management. A fourth option, such as pyrolysis (thermochemical process to convert sludge to biosolids), would improve the stability of the industry but requires a large capital cost.
- PFAS contamination may create problems for incineration and landfilling of biosolids as well as land application.
- Environmental justice implications should be considered for incineration and for land application. The synergistic impacts of other constituents on vulnerable communities further compounds the issue.
- Any regulatory limits for PFAS need to be considered within the context of background PFAS levels in the environment and exposure to PFAS from sources other than biosolids.

NPDES & Pretreatment Programs


UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

December 5, 2022

MEMORANDUM

SUBJECT: Addressing PFAS Discharges in NPDES Permits and Through the Pretreatment Program and Monitoring Programs

FROM: Radhika Fox
Assistant Administrator

TO: EPA Regional Water Division Directors, Regions 1-10

The National Pollutant Discharge Elimination System (NPDES) program is an important tool established by the Clean Water Act (CWA) to help address water pollution by regulating point sources that discharge pollutants to waters of the United States. Collectively, the U.S. Environmental Protection Agency (EPA) and states issue thousands of permits annually, establishing important monitoring and pollution reduction requirements for Publicly Owned Treatment Works (POTWs), industrial facilities, and stormwater discharges nationwide. The NPDES program interfaces with many pathways by which per-and polyfluoroalkyl substances (PFAS) travel and are released into the environment, and ultimately impact water quality and the health of people and ecosystems. Consistent with the Agency's commitments in the October 2021 *PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024 (PFAS Strategic Roadmap)*, EPA will work in cooperation with our state-authorized permitting authorities to leverage the NPDES program to restrict the discharge of PFAS at their sources. In addition to reducing PFAS discharges, this program will enable EPA and the states to obtain comprehensive information on the sources and quantities of PFAS discharges, which can be used to inform appropriate next steps to limit the discharges of PFAS.

In December of 2022, the USEPA issued a memorandum entitled "PFAS Discharges in National Pollutant Discharge Elimination System (NPDES) Permits and Through the Pretreatment Program and Monitoring Programs". It gives recommendations for PFAS monitoring and, in some specific cases, enforcing PFAS limits for wastewater and stormwater NPDES permits and industrial pretreatment programs, through general 40 CFR regulations for pollution prevention. Enforcement of these permits and programs is commonly done by states and POTWs.

The memo directly addresses biosolids in paragraph C, which is pasted below with author notes in brackets [ ].

C. Recommended Biosolids Assessment

1. Where appropriate, states may work with their POTWs to reduce the amount of PFAS chemicals in biosolids, in addition to the NPDES recommendations in Section B [Recommendations for POTWs] above, following these general steps:

a. EPA recommends using draft method 1633 to analyze biosolids at POTWs for the presence of 40 PFAS chemicals.
b. Where monitoring and IU [Industrial User] inventory per section B.2 [Effluent-and wastewater residuals monitoring] and B.3.a [Update IU Inventory] above indicate the presence of PFAS in biosolids from industrial sources, EPA recommends actions in B.3.b [Utilize Best Management Practices and Pollution Prevention to address PFAS Discharges to POTWs] to reduce PFAS discharges from IUs.
c. EPA recommends validating PFAS reductions with regular monitoring of biosolids. States may also use their available authorities to conduct quarterly monitoring of the POTWs (see 40 CFR 403.10(f)(2)) [State Pretreatment Program Requirements, Procedures].

State Regulations

Every state must follow federal regulations, including 40 CFR 503 “Standards for the Use or Disposal of Sewage Sludge”. However, as explained in the previous section, there are no regulations for PFAS in biosolids, only recommendations in a 2022 USEPA memorandum. So many states are taking a proactive approach by creating their own regulations.

Table 6 provides a summary of current and pending regulations by state. Note that several states are considering adding or changing their regulations, so this table may not reflect the latest state requirements. For the latest regulations, visit the state’s environmental department website (State EPA, DEQ, DEP, or DNR).

Highlights of state regulations:

- **Maine** is the only state with a total ban on the land application of biosolids.
- **Massachusetts** requires that biosolids/residuals approved for land application monitor for PFAS on a quarterly basis for water treatment solids, paper sludge, and industrial sludge.
- **Michigan** has monitoring requirements for PFAS in land applied biosolids and prohibits the application of biosolids deemed to be industrially impacted. The following limits are imposed for a common PFAS compound, PFOS:
  - If PFOS is above 125 parts per billion (ppb), land application is prohibited.
  - If PFOS is between 50 ppb and 125 ppb, the application rate must be at or below 1.5 dry tons per acre (dt/acre). A typical biosolids rate 3.0 dt/acre.
  - If PFOS is below 50 ppb there is no limitation

  Michigan also has pretreatment standards for PFAS which typically reduces PFAS in POTW biosolids.
- **New Hampshire** requires facilities to monitor PFAS in Sludge Quality Certificate (SQC) biosolids (Classes A or B). New Hampshire also plans to issue a soil standard for PFAS that can be used to calculate a sludge loading limit and to restrict certain land applications.
- **Vermont** requires PFAS monitoring in biosolids, soils, groundwater, and crops at land application sites.
- Several states have cities, counties, municipalities, districts, or other jurisdictions with their own regulations related to biosolids disposal or land application and PFAS, including Arizona, Colorado, Massachusetts, Michigan, Minnesota, New Hampshire, North Carolina, Tennessee, and Texas.

Table 6: States with Regulations on PFAS in Biosolids, as of January 2024 (X = Adopted, P = Legislation Proposed)

States	Land Application Requirements				PFAS Monitoring for all Biosolids	PFAS Source Assessment	Jurisdictions with Special Rules	Other
	Complete Ban	Land Use Restricted	PFAS Limits	PFAS Monitoring				
Arizona							X	
California					X			
Colorado				X		X	X	
Connecticut					Industrial			
Florida					Industrial	X		
Illinois					P	P		
Iowa					P			
Maine	X			X		X		
Maryland				X				
Massachusetts			P	X			X	Product labels
Michigan		X	X	X	Industrial	X	X	Pretreat limits
Minnesota				P	P	P	X	
Nevada					Industrial			
New Hampshire		X	P	X	X	X	X	
New Jersey				P	P	P		WW monitoring
New York		X	P	X	X	X		Recycling focus
North Carolina							X	
Oklahoma		P		P	P			Product labels
Oregon				P				
Pennsylvania		X		X				
South Carolina				X				
Tennessee							X	
Texas							X	
Vermont				X	X			
Virginia					P	P		
Washington		P	P	P	P			
Wisconsin					P			Study underway

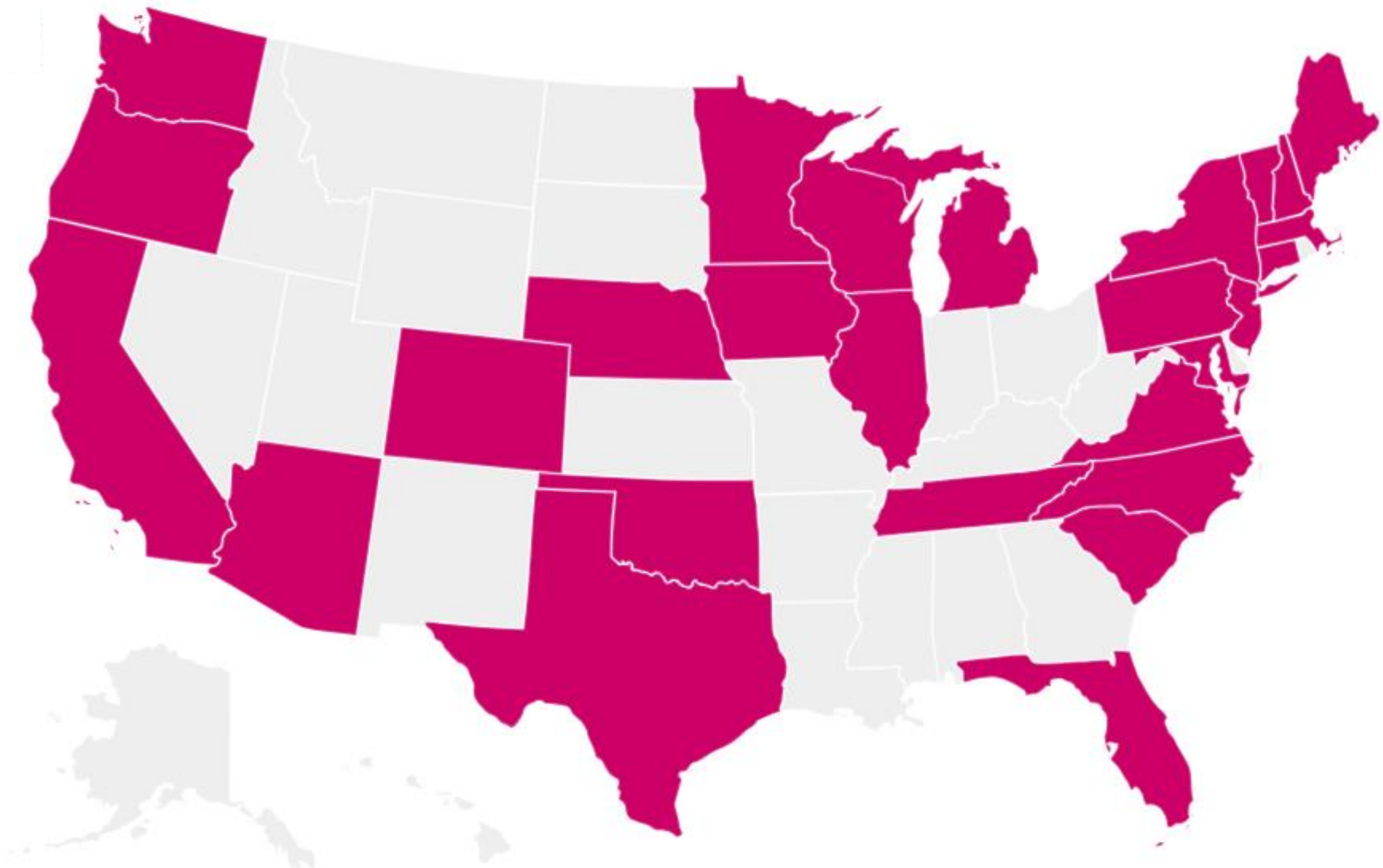


Figure 17: States will PFAS in biosolids related regulations.

Lab Test Method

The USEPA has recommended Draft Method 1633 as a laboratory-validated method for testing for PFAS in biosolids. With this method, solid samples are spiked with isotopically labeled standards, extracted into basic methanol, cleaned up by carbon and solid phase extraction (SPE) cartridges, then liquid chromatography with tandem mass spectrometry (LC-MS/MS) analyzes the PFAS compounds extracted from the solids. It is a complex test as shown in Figure 18.

Method 1633 includes these key features:

- Testing can be done with a variety of samples including wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and animal tissue.
- Measures up to 40 different PFAS compounds.
- Detects low levels of PFAS (ppt).
- Reliable and accurate.
- Cost around $125 per test as of January 2024.
- Takes around 20 to 30 minutes.

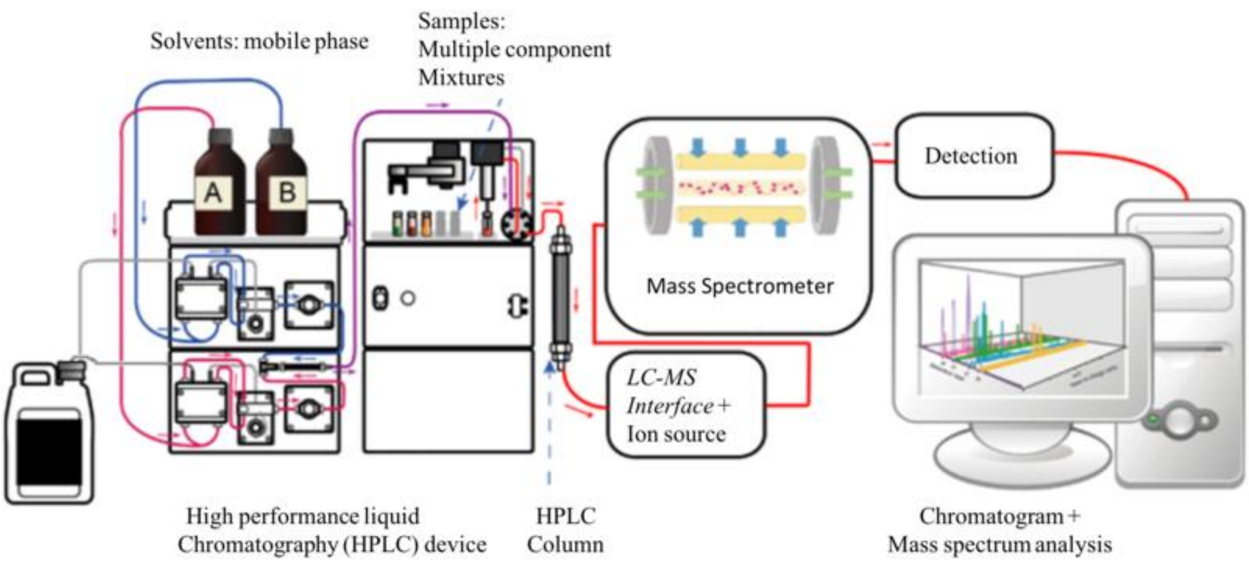


Figure 18: Diagram of an LC-MS/MS testing setup similar to that used for Method 1633.
Source: commons.wikimedia.org/wiki/File:Liquid_Chromatography_Mass_Spectrometer.png, Public Domain

PFAS Removal, Destruction & Stabilization

It is difficult and expensive to remove or destroy PFAS in biosolids. It is more effective to find the sources of PFAS and prevent them from entering the wastewater and biosolids. The next most effective approach is to remove the PFAS from the wastewater such that it does not enter the biosolids.

PFAS Removal in Wastewater

PFAS removal from liquid wastewater can be done with the following techniques:

- Granular Activated Carbon (GAC) Adsorption
  - Creates a solid waste
- Ion Exchange (IX)
  - Creates a liquid regeneration waste
- Nano-Filtration (NF) or Reverse Osmosis (RO)
  - Creates a liquid concentrate
- Advanced Oxidation Processes (AOP)
  - Ultraviolet radiation (UV) with hydrogen peroxide (H_2O_2), see Figure 19
  - Ozone and peroxide
  - Heat-activated persulfate

Most PFAS removal techniques produce a waste byproduct containing PFAS. Managing and disposing of this waste can be expensive. AOP processes have the potential to break down and destroy the PFAS compounds such that there is no PFAS containing waste byproduct.

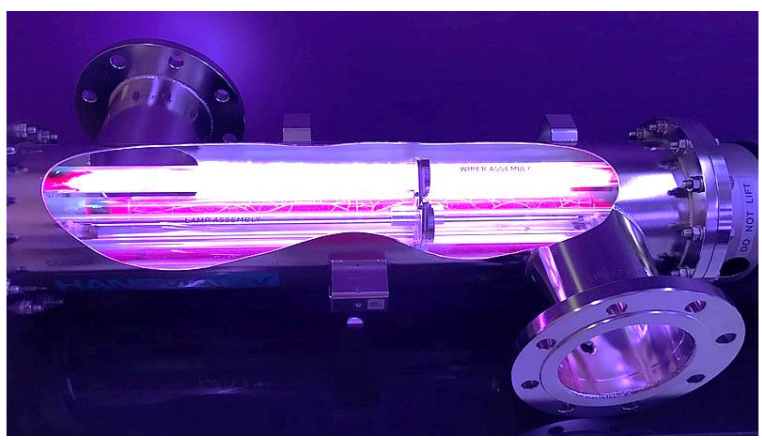


Figure 19: UV lamps in a pipe. Injecting H_2O_2 upstream allows for PFAS destruction.
Source: wikimedia.org/wiki/File:Cutaway_model_of_UV_disinfection_unit_used_in_NEWater_water_treatment_plants.jpg, Z22

PFAS Destruction in Biosolids

Complete destruction of PFAS is called mineralization, which is the complete defluorination of PFAS. The final products of mineralization include carbon dioxide, water, hydrogen fluoride, and/or sulfur molecules. As mentioned above, AOP processes can destroy PFAS in liquid wastewater before sludge and biosolids are created.

Conventional sludge treatment techniques have minimal impact on degrading or destroying PFAS. These techniques include thickening, dewatering, pelletization, alkaline stabilization, aerobic digestion, and anaerobic digestion. Some techniques such as digestion result in polymer or long-chain PFAS breaking down into multiple short-chain PFAS. However, this does not significantly reduce the total PFAS concentration.

PFAS destruction of biosolids with PFAS can be obtained through incineration. Conventional municipal incinerators typically operate at temperatures between 980°C and 1200°C, which is theoretically sufficient to destroy organic compounds including all types of PFAS. However, studies have shown that conventional incineration actually doesn't completely destroy all PFAS. Testing of stack emissions has shown that a small portion of PFAS gets released into the air. Modifications to conventional incineration can result in a more complete destruction of PFAS in biosolids. Note that incineration of biosolids with PFAS can emit a small amount of air pollutants, such as fluorinated greenhouse gases.

Figure 20: Solid waste combustion on a moving grate incinerator at a municipal waste-to-energy plant. Temperatures become high enough for the defluorination of PFAS.
Source: commons.wikimedia.org/wiki/File:Movinggrate.jpg, public domain

PFAS Stabilization

The goal of PFAS stabilization is to attach PFAS compounds to large stable particles called sorbents, so they are unlikely to transport into the environment and harm wildlife or people. Although not destroyed, the stabilized PFAS are no longer harmful for the foreseeable future. Biosolids with stabilized PFAS can be disposed of at a landfill with a low risk of PFAS leaching into the environment. And they can be land applied with less likelihood of PFAS entering plants, animals, or groundwater.

PFAS stabilization in biosolids can be achieved by adding and mixing any of the following sorbents:

- Activated carbon,
- Clay minerals,
- Biochar,
- RemBind® proprietary mix, or
- Mixtures of carbon powder and minerals.

Figure 21: Biochar (left) and activated carbon (right) which can be mixed with biosolids.

Source: https://commons.wikimedia.org/wiki/File:Crushed_biochar.jpg, GIZ Bush Control and Biomass Utilisation Project commons.wikimedia.org/wiki/File:Activated_carbon_A.jpg, Aariuser I, CC-BY-SA-2.0

Disposal Costs

Biosolids handling and disposal can be significant ongoing operations costs for wastewater systems, even without any consideration for PFAS. Table 7 shows example biosolids disposal costs, although these values vary greatly by location. The values here are for comparative purposes only.

Table 7: Example Biosolids Disposal Costs

Disposal Method	Cost per Wet Ton Biosolids	Annual Cost for 3 MGD WWTP	Assumptions and Notes
Hauling	$80	$2.2M	5 miles with tanker or trailer, once a day
PFAS Stabilization	$50	$1.4M	Assumes mixing activated carbon into sludge
Land Application	$40	$1.1M	Mostly tractor & labor costs; Not including hauling
Landfill	$65	$1.8M	Tipping fees; Not including hauling
Incineration	$120	$3.3M	Can destroy PFAS; Not including hauling

Example Problem 5

Based on Table 7, rank the following biosolids options in terms of cost per ton:

- Hauling and Land Application
- Hauling, Stabilization, and Land Application
- Hauling and Landfill
- Hauling and Incineration

Solution:

Ranked with one being the lowest cost per ton:

1. $120 - Hauling and Land Application
2. $145 - Hauling and Landfill
3. $170 - Hauling, Stabilization, and Land Application
4. $200 - Hauling and Incineration

Helpful References

USEPA:

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