November 2017 DRAFT Per- and Poly-Fluorinated Alkyl Substances Chemical Action Plan (PFAS CAP)

The Washington State departments of Ecology and Health prepared additional sections for the draft PFAS CAP for external review. The biosolids section may be modified in response to comments and the content re-organized for the draft Interim PFAS CAP.

The 2017 Draft Interim PFAS CAP includes:

- Health, Environment, Chemistry, Regulations – posted online 09/20/2017
- Uses, Intro – posted online 10/05/2017
- Sections on Ecological Receptors and Biosolids - posted online 11/08/2017

The draft chapters and sections may include cross-references to other sections/chapters in the Draft Interim PFAS CAP or notes where additional information will be provided in a later draft.

Ecology and Health are asking interested parties to provide feedback on these draft documents by **November 17, 2017.**

Submit comments, suggestions, and questions to Kara Steward at kara.steward@ecy.wa.gov

The Draft Interim PFAS CAP documents are posted at https://www.ezview.wa.gov/?alias=1962&pageid=37105 (at the bottom of the webpage).

BACKGROUND

Amendments to the Federal Water Pollution Control Act of 1948, which became commonly known as the Clean Water Act (1972), set in motion the creation of wastewater treatment across the US. Large scale construction of wastewater treatment plants (WWTPs) was initiated in 1972 when these facilities were nationally funded under a grant program administered by EPA.

One of the primary functions of wastewater treatment is to remove solids from the influent. Treatment plants utilize a variety of engineering designs, but most employ some sort of biological treatment whereby aquatic bacteria consume, i.e. digest, the organic constituents in the influent. The biological/organic floc along with mineral & chemical constituents are settled out of the wastewater prior to discharge of effluent. Typically, these solids are mechanically dewatered. Some facilities in arid climates air-dry the solids as a primary method of dewatering or in addition to a mechanical process.

In Washington, biosolids are land applied for their nutrient and soil amending properties. Land application of biosolids is conducted almost exclusively in conjunction with commercial farming operations across the state. Department of Ecology approves individual biosolids applications on an agronomic basis—matching nitrogen needs of the crop with that supplied by biosolids. Analysis of both soil and biosolids is required by rule to calculate site specific rates in advance of application.

FEDERAL AND STATE REGULATION

EPA administers the federal rule (40 CFR Part 503) under which specific sampling, analysis, and management is required of WWTP residuals.. Under '503' the solids generated by wastewater treatment are termed "sewage sludge".

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Washington regulation (Chapter 173-308 WAC-Biosolids Management) differentiates between wastewater solids that meet the regulatory standards, classified as "biosolids", and those solids not meeting the standards which are defined as "sewage sludge". Washington law requires that biosolids are land applied to the greatest extend possible, but that sewage sludge be disposed in a landfill. Currently, about 85-90% of biosolids generated in Washington are land-applied.

Washington's biosolids rule adopts all the standards in the federal rule regarding sampling and analysis of wastewater treatment solids. It imposes additional management criteria related to site evaluation and permitting, development of management plans that govern the land application procedures, and ongoing oversight/approval of application rates and operations.

ASSESSMENT OF BIOSOLIDS RISK

EPA developed the federal rule after undertaking a substantive 9-year evaluation of sewage sludge land application. This process included an "extensive multi-pathway risk assessment for evaluating and setting limits to manage pollutants in biosolids" (1). It involved making a list of pollutants, developing risk-assessment methodologies, determining pollutant limits & management practices, and issuing the rule.

In 1984 EPA identified a list of 200 potential pollutants in wastewater residuals for evaluation. A scientific panel reviewed this list and made a recommendation that approximately 50 of these pollutants be evaluated for further study. The evaluation considered toxicity, occurrence, and fate and effects of the pollutants. However, perfluorooctane sulfonate (PFOS) and perfluoroctanoic acid (PFOA) were not on this list and thus not evaluated.

The National Academy of Sciences (NAS) has twice reviewed the federal rule. In 1996 the NAS released "Use of Reclaimed Water and Sludge in Food Crop Production" and in 2002 reviewed the science and methodology underlying the health and environmental standards entitled "Biosolids Applied to Land: Advancing Standards and Practices". Both studies concluded that the federal rule was protective of human Health and the environment, but PFOS and PFOA were not specifically part of the evaluations. The 2002 NAS review stated that "there is no documented scientific evidence that the Part 503 rule has failed to protect health".

WWTP RESIDUALS (BIOSOLIDS & SEWAGE SLUDGE) ANALYSIS & CONCENTRATIONS

The required analytes and analytical methods for WWTP residuals in the US are specified by EPA in the federal rule (40 CFR Part 503) and incorporated into the Washington state rule (Chapter 173-308 WAC). Regulatory analysis in Washington is required to be conducted by laboratories accredited by the Department of Ecology. Among many pollutants, PFOS and PFOA are not specifically regulated by the federal or state rules that apply to wastewater treatment residuals.

The chemistry of biosolids is often reflective of the chemistry of our daily lives as is the dust in our homes [2]. Washington residents are exposed to PFOS/PFOA from carpets, food packaging, surface coatings on textiles, GorTex fabric, ski wax, and wide variety of other sources. Toxic chemicals that are washed down the drain from sinks, toilets and washing machines often end up in the biosolids.

EPA has approved a PFOS/PFOA analysis method for drinking water, Method 537 [3], and has a draft procedure (published in 2011) for biosolids analysis published using high performance liquid chromatography (HPLC) combined with tandem mass spectrometry [4]. Soil analysis may be conducted by using ASTM Method D7968 with detection limits of 18.83 ng/kg and 6.24 ng/kg for PFOS and PFOA respectively.

The concentration of PFOS/PFOA in biosolids has been reported from a variety of sources outside of Washington State [5, 6, 7, 8, 9, & 10] with PFOS often being the most abundant [6, 10], probably reflecting the more prevalent use of PFOS at the time the studies were conducted. There is no known data from analysis for PFOS/PFOA in biosolids generated in Washington State. Four WWTPs in Washington had effluent analysis for PFOS/PFOA, but this review did not include an analysis of biosolids for these compounds [11].

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Industrial sources of perfluoroalkylates can influence concentrations of these compounds in biosolids when a wastewater treatment plant receives influent directly from industries that work with fluorotelomer compounds. A WWTP in Decatur, Alabama received effluent from industries that conducted electrochemical fluorination and worked with a variety of fluorotelomer compounds and perfluoroalkylates (12). The data for PFOA concentrations from Decatur sludge are fragmentary, but show high levels in years 2005-6: 528 ng/g & 683 ng/g in 2005, and 1875 ng/g in 2006 (12). Subsequent to significant reduction in perfluorocarboxylates from industrial discharges, concentration of PFOA in the Decatur biosolids decreased markedly. Data available from Decatur biosolids produced in 2008 indicate PFOA concentrations in biosolids of 27 & 32 ng/g (13).

Washington State does not have commercial production of perfluorochemicals and industrial discharges are separated from domestic wastewater treated at the 300 + wastewater treatment plants in the state that produce biosolids for land application. There may be manufacturers who use PFAS in their processes but these are not known to the state at this time.

Archived samples of biosolids from the EPA National Sewage Sludge Survey in 2001 were combined into 5 composite samples and analysis showed concentrations of PFOS at 403 +/- 127 ng/g, and PFOA at 34 +/- 22 ng/g, (7). These data represented 94 WWTPs in 32 states, but did not include Washington State.

Comparison of data from the National Health & Nutrition Examination Surveys (NHANES) in 1999-2000 and 2003-4 indicate a reduction in PFOS and PFOA levels in human blood (14). They conclude this is "most likely related to discontinuation in 2002 of industrial production…of PFOS and related perfluorooctanesulfonyl fluoride compounds".

This trend of reduced concentration of PFOA/PFOS is also observed across a broad spectrum of data characterizing biosolids. A review of sewage sludge analysis in Germany evaluated perfluoroalkyl acids (PFAAs) concentration from 4981 samples from 1165 WWTPs collected between 2008 and 2013 (9). Seventy-one WWTPs had samples exceeding an EU precautionary level of 125 ug/kg, but this occurred with decreasing tendency over time. The exceedances decreased from 6% in 2008 to 0.8% in 2013 and WWTPs uncontaminated with PFOS/PFOA increased by 32%. In the samples evaluated, PFOS was found in 41% and PFOA in 7%. 47% of WWTPs showed clear decreases over time and 16% showed an increasing trend. The total load of PFAAs in sewage sludge was reduced by over 90% during this time period.

A summary of perfluorinated compounds (PFCs) in sewage sludge from 2005-2015 monitoring data worldwide was compiled by carbon chain length at concentrations of ng/g (10). With few exceptions, these data are lower for PFOS & PFOA than the composite results from samples in the EPA National Sewage Sludge Survey of 2001.

EFFECTS OF BIOSOLIDS LAND APPLICATION

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Biosolids from the Decatur WWTP (referenced above) were land applied to about 2000 ha of agricultural fields for over a decade. The elevated levels of perfluoroalkylates (PFAs) in the biosolids generated concern that land application may constitute a pathway to contaminate surface and ground water. In order to evaluate this risk, EPA collected some initial soil samples in 2007 from Decatur land application sites and from nearby “background” fields. Results indicated the presence of high concentrations of several fluorotelomer alcohols (FTOHs) and PFAs in soil [12]. After collection of these initial soil samples and public drinking water samples, EPA collected an expanded set of soil samples in 2009 to more accurately characterize the extent of contamination in and around the land application sites. [15, 16, 17].

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The soil from sludge-applied fields in Alabama had perfluoroalkylate concentrations that were higher than in background field samples. The highest PFOA concentrations from sludge-applied fields ranged up to 320 ng/g and PFOS ranged up to 410 ng/g [12]. Annual biosolids application rates of Decatur biosolids for a 5-year period between 2002 and 2006 ranged from 14.9 to 43.9 Mg/ha [16]. These rates are well above Washington’s mean application rate approval of 6.95 Mg/ha. This mean value is based on 809 regulatory approvals for land application of biosolids for Alfalfa/grass hay, barley, canola, corn, hops, sunflowers, triticale, & wheat over the years 2010 to 2017 for which data is available [18]. The Decatur rates exceed all but 6 of the 809 Washington approvals. The six higher land application rates were for lagoon biosolids that contained significant amount of mineral material (sand) and low nitrogen content. From the perspective of an agronomic evaluation, rates used for the Decatur biosolids would have likely resulted in excessive N accumulations and leaching of nitrate. Such rates would be unlikely to receive regulatory approval in Washington.

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There is evidence that PFOS/PFOA persistence in soil is related to carbon chain length with longer carbon chains being more persistent. Short chains are more mobile in soil[6, 12]. Smaller chain congeners, or what has been described by some as precursors, may combine into longer chains [6].

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The sorption of perfluorinated compounds to soil influences their fate and distribution in the environment after land application. Determining partition coefficients that are reflective of the environmental fate of these compounds has proven difficult. Laboratory derived values appear to differ from gross distribution of perfluorinated compounds in the environment. Lab-based Log K_{oc} values may overestimate PFOS/PFOA concentrations in water and underestimate soil residence time [8].

In 2010?, municipal biosolids from Chicago were land applied to investigate questions about the fate of perfluorochemicals [6]. This investigation indicated four significant results: Concentrations of PFCs in soil increased linearly with increasing biosolids loading rate (PFOS 2-483 ng/g), desorption experiments indicated that the leaching potential of perfluorochemicals decreased with increasing carbon chain length, previously derived organic carbon partition

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coefficients may not be accurate predictors of the desorption of long-chain PFCs, and trace levels of short-chain PFCs were detected in soil cores below the level of incorporation.

The loading rates in the Sepulvado investigation using Chicago biosolids [6] were significantly higher than the mean Washington agronomic rate of 6.95 Mg/ha [18]. Sepulvado reported cumulative loading rates in their long-term plots (applications over 32 years) to be 553 Mg/ha (low rate), 1109 Mg/ha (medium rate) and 2218 Mg/ha (high rate). It would require 79, 159, and 319 years of annual applications respectively at Washington's mean application rate (6.95 mg/ha) to achieve similar cumulative loading. Specific data, however, are unavailable about levels of PFAS in Washington fields with biosolids application.

Most fields in Washington do not have biosolids applied annually. On wheat/fallow rotations applications are made every other year at most, and commonly every 4th year.

In 2009 EPA developed residential soil screening guidance values for PFOS at 6 mg/kg (6,000 ug/Kg) and PFOA at 16 mg/kg (16,000 ug/kg) [19]. In order to estimate the time (in years) to reach the cumulative loading in EPA's guidance, it's necessary to know the concentrations of PFOS/PFOA in the biosolids, the annual application rate in Mg/ha, and the dilution factor used, i.e. the soil depth. No known concentration data for PFOS/PFOA in Washington biosolids is currently available.

TABLE 1: ***Comparative estimates of the time needed to reach EPA's soil guidance concentrations from annual applications of biosolids using various concentration estimates and mean Washington application rate (6.95 Mg/ha).***

Biosolids PFOS[a]/PFOA[b] Concentration	Biosolids Application Rate[18]	PFOS/PFOA Applied per Application-Dry Weight	Soil Depth	Soil Weight	Calculated Soil Conc.	EPA Guidance Levels	Years To Reach EPA Levels*
19/10 ug/kg ***Ulrich*** [9]	6.95 mg/ha	[a]132,050 ug [b]69,500 ug	15 cm	2,000,000 kg	0.066 ug/kg 0.035 ug/kg	6,000 ug/kg 16,000 ug/kg	[a] 90,909 [b]457,142
32 ug/kg PFOA ***Wash.*** [12]	6.95 Mg/ha	220,400 ug	15 cm	2,000,000 kg	0.111 ug/kg	16,000 ug/kg	[b]144,144
403/34 ug/kg ***EPA Composites 2001*** [7]	6.95 Mg/ha	[a]2,800,850 ug [b] 236,300 ug	15 cm	2,000,000 kg	1.396 ug/kg 0.118 ug/kg	6,000 ug/kg 16,000 ug/kg	[a]4,298 [b]135,593

* One application annually, summed empirical amounts only (No formation, degradation or leaching of PFOS/PFOA)

PERFLUOROCHEMICAL PRODUCTION EFFECT ON BIOSOLIDS

PFOS was voluntarily phased-out of production in the US between years 2000-02 by its primary producer 3M Company [20]. Since 2006, eight global manufacturers have been participating in a

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voluntary phase-out of PFOA with a goal of elimination by 2015 [21]. Reduced production of PFOS & PFOA is likely the reason for the lower concentrations of these chemicals in sewage sludge and biosolids in recent years. These chemicals have been replced by short chains in many uses.

Given the data from PFOS/PFOA analysis of WWTP residuals outside of Washington it's likely these compounds are present in biosolids generated in Washington State and that concentrations vary depending on WWTP. The phase-out of PFOS & PFOA by manufacturers along with the PFOS/PFOA data trends in Germany [9] and locations worldwide [10] suggest that concentrations of these chemicals are likely to be low and trending downward in Washington biosolids. Biosolids are applied to less than 1% of the state's farmland on an annual basis.

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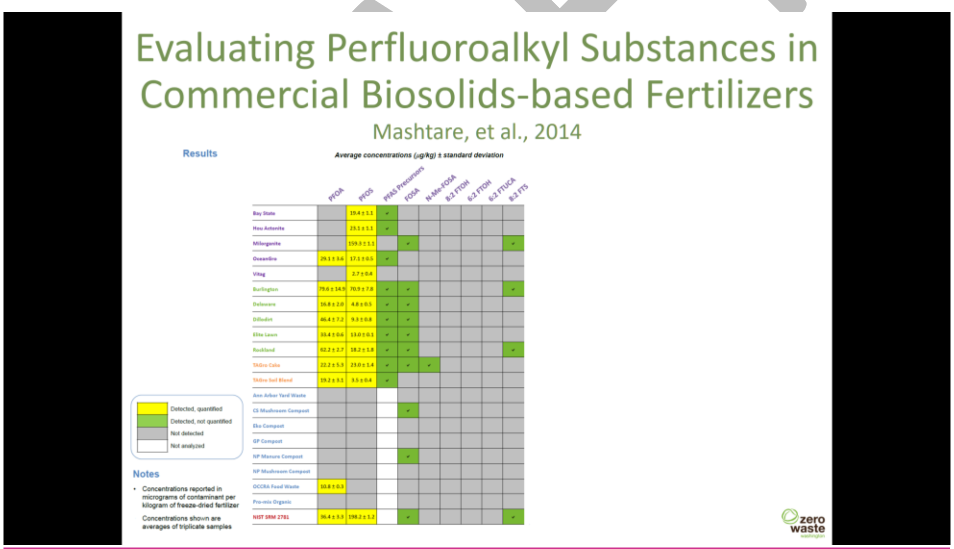

	PFOA	PFOS	PFAS Precursors	FOSA	N-Me-FOSA	8:2 FTOH	6:2 FTOH	6:2 FTUCA	8:2 FTS
Bay State		19.4 ± 1.1	✓						
Hou Actonite		23.1 ± 1.1	✓						
Milorganite		159.3 ± 1.1		✓					✓
OceanGro	29.1 ± 3.6	17.1 ± 0.5	✓						
Vitag		2.7 ± 0.4							
Burlington	79.6 ± 14.9	70.9 ± 7.8	✓	✓					✓
Delaware	16.8 ± 2.0	4.8 ± 0.5	✓	✓					
Dillodirt	46.4 ± 7.2	9.3 ± 0.8	✓	✓					
Elite Lawn	33.4 ± 0.6	13.0 ± 0.1	✓	✓					
Rockland	62.2 ± 2.7	18.2 ± 1.8	✓	✓					✓
TAGro Cake	22.2 ± 5.3	23.0 ± 1.4	✓	✓	✓				
TAGro Soil Blend	19.2 ± 3.1	3.5 ± 0.4	✓						
Ann Arbor Yard Waste									
CS Mushroom Compost				✓					
Eko Compost									
GP Compost									
NP Manure Compost				✓					
NP Mushroom Compost									
OCCRA Food Waste	10.8 ± 0.3								
Pro-mix Organic									
NIST SRM 2781	96.4 ± 3.3	198.2 ± 1.2		✓					✓

REFERENCES

(1) EPA publication 832/B-93/005: Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule;

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Deleted: en actual application timing & rates, combined with likely biosolids PFOS/PFOA concentrations, the risk to human health and the environment from biosolids land application in Washington appears to be low.

(2) Hundal, et al, Evaluating Exposure Risk to Trace Organic Chemicals in Biosolids, BioCycle, August, 2011;

(3) Technical Advisory-Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1;

(4) EPA Draft Procedure for Analysis of Perfluorinated Carboxylic Acids and Sulfonic Acids in Sewage Sludge and Biosolids by HPLC/MS/MS, December 2011;

(5) Loganathan et al, Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia, Water Research, Vol. 41, Issue 20, December 2007;

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(7) Arjun Venkatesan & Rolf Halden, National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey, Journal of Hazardous Materials 2013, 413-418;

(8) Zareitalabad et al, Perfuorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils, and wastewater—A review on concentrations and coefficients, Chemosphere 91, 2013, 725-732;

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(13) Washington et al., Supporting Information for: Concentrations, distribution and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA, Office of Pollution Prevention and Toxics, EPA, 2010.

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(14) Calafat, et al, Polyfluoroalkyl Chemicals in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003-2004 and Comparisons with NHANES 1999-2000. Environmental Health Perspectives, vol. 115, No. 111, November 2007;

(15) Organic Consumers Association--https://www.organicconsumers.org/news/epa-finds-record-pfos-pfoa-levels-alabama-grazing-fields;

(16) Northeastern University --https://pfasproject.com/decatur-alabama/;

(17) Florida Action Newwork-- http://fluoridealert.org/news/alabama-pfoa-contaminated-sludge-spread-in-lawrence-county/

(18) Washington Department of Ecology biosolids land application data, GIS data summary, Severtson, July 2017;

(19) Soil Screening Levels for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS), 2010;
https://archive.epa.gov/pesticides/region4/water/documents/web/html/pfcdaltonindex.html

(20) EPA Fact Sheet, PFOA & PFOS Drinking Water health advisories, EPA 800-F-16-003, November 2016;

(21) EPA Fact Sheet: 2010/2015 PFOA Stewardship Program (https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program)