

March 2, 2023

Mark Gordon
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Subject: Comments on Draft PFAS Guidance for Investigating and Remediating PFAS Contamination in Washington State

Dear Mr. Gordon:

Thank you for the opportunity to provide comments on the Draft *PFAS Guidance for Investigating and Remediating PFAS Contamination in Washington State* prepared by the Toxics Cleanup Program, Washington State Department of Ecology (Ecology).

Our comments on the draft guidance are provided on the following pages. If you have any questions, please do not hesitate to reach out.

Sincerely,



Cindy Bartlett, LG
Principal Geologist



Jason Conder, Ph.D., IBERAD
Principal

COMMENTS ON DRAFT ECOLOGY PFAS GUIDANCE DOCUMENT

CHAPTER 2. Potential Human Health Effects, Groundwater Impacts, and Regulations

General Comment: Additional Key Matrices

Additional matrices including landfill leachates, wastewater, and sediments are not addressed in the cleanup criteria. Could this document be used as a tool of reference for non-drinking water matrices? Criteria for additional matrices are necessary given the increasing number of identified per and polyfluoroalkyl substances (PFAS) sources and should be added in this guidance document.

General Comment: Consideration of Sulfonamide and Sulfonamido Acetic Acid-Based PFAS

Though not currently regulated at state or federal levels, it may be worthwhile to consider the fate/transport and toxicological risks of electrochemically fluorinated PFAS such as sulfonamide- or sulfonamido acetic acid-based PFAS (e.g., perfluorooctane sulfonamide [PFOSA] or methylperfluorooctane sulfonamido acetic acid [N-MeFOSAA], which are included in EPA method 1633. These classes of PFAS are characterized by a more neutral acid dissociation constant (pKa) compared to the other common perfluoroalkyl acids (PFAAs), which influence partitioning and distribution between soil and groundwater and will affect impacts on toxicological endpoints (Rayne and Forest, 2009; Rericha et al., 2022).

General Comment: Transition to Fluorine-Free Foams

Chapter 2 provides a good overview of PFAS-polluted sites in Washington, mainly attributed to aqueous film-forming foam (AFFF) releases. The United States military is required to transition to PFAS-free firefighting foams by October 2023, per the National Defense Authorization Act of 2020. The Department of Defense (DoD) is required to stop using all PFAS-based foam by October 2024.

We suggest referencing Ecology's work on AFFF phase-out regulations and clarifying the role of the Department of Ecology in the effort to transition to fluorine-free foams (DOE, n.d.).

CHAPTER 3. Advisory, Action, and Cleanup Levels, and Historical Investigatory Levels

Section 3.2: Establishing MTCA Cleanup Levels, page 13

This section mentions: *“While final cleanup levels for a site will be established in the Cleanup Action Plan, it helps to set preliminary cleanup levels early in the cleanup process so all parties have a common understanding of the potential severity of contamination that might be found during the site investigation.”*

We recommend adding information regarding how and when to use preliminary cleanup levels. For instance, can they be used for compliance considering that they are preliminary? Is there any qualitative severity scale (H/M/L) based on extent and levels of contamination?

The rapidly changing preliminary cleanup levels create uncertainty in the applicability of these values.

Subsection 3.2.3: Potable Groundwater Cleanup Levels, page 17

This subsection mentions: “*Ecology expects that the SALs will be considered ARARs and therefore applied as the cleanup levels at sites where groundwater is currently being used, or may be used in the future, as a potable drinking water source.*”

The sentence concludes that the established State Action Levels (SALs) pertain to potable drinking water. Please, clarify if the established SALs can be used for non-potable water, as suggested on page 16, and if they can be used for other matrices such as wastewater.

Subsection 3.2.4: Surface Water Cleanup Levels, page 18

This subsection states “*However, these calculations can’t be performed because chemical-specific BCFs are not available at this time for any PFAS.*” Bioconcentration factors (BCFs) are available from laboratory studies for many PFAS and can be used to support calculations of surface water cleanup levels based on fish or shellfish consumption. Reviews of BCF values for PFAS can be found in Burkhard et al. (2021) and Conder et al. (2021).

Subsection 3.2.5: Soil Cleanup Levels, page 21

The following comments refer to the PFAS soil concentrations that are estimated to be protective of potable groundwater listed in Table 5 and estimated using Model Toxics Control Act (MTCA) equation 747-1:

1. Does Ecology have plans to generate more site-specific cleanup levels for more specific regional soil types as opposed to the generalized “default soil characteristics” mentioned on page 20? Small variations in soil properties can significantly influence PFAS retention and release (Minh Hong Nguyen et al., 2020; Barzen-Hanson et al., 2017).
2. Branched and linear isomers of certain PFAS have been shown to have significantly different retention and transport characteristics under both saturated and unsaturated conditions (Schulz et al., 2020; Stults et al., 2022). Are there plans to differentiate between branched and linear isomers during analytical analyses and/or soil cleanup recommendations?
3. The current MTCA equation 747-1 does not account for PFAS partitioning to the air-water interface, which can retain a significant proportion of PFAS in soil (Brusseau et al., 2019). Inclusion of an estimate of PFAS partitioning to the air-water interface would improve soil screening levels. Though more comprehensive models are being researched and published, two equations which can currently be found in the literature are listed below (Equations 1 and 2):

$$\text{Log} (K_{ia}) = (0.020 * V_m) - 8.2 \tag{1}$$

where V_m is molar volume in cubic meters per mol (cm^3/mol) and K_{ia} is air-water partitioning coefficient in cm^{-1} (Brusseau et al., 2019).

$$K_{ia} = 7.84 * 10^{-6} e^{.427 * C18Rt} \tag{2}$$

Table 1. Comparison of soil concentrations protective of potable groundwater listed in Table 5 to EPA method 1633 draft 3 minimum levels of quantitation.

PFAS	Vadose zone	Saturated zone	Units	1633 ^a ML ^b (mg/kg)	Vadose zone	Saturated zone
PFOA	6.3E-05	4.0E-06	mg/kg	2.00E-04	Below ML	Below ML
PFOS	1.7E-04	9.9E-06	mg/kg	2.00E-04	Below ML	Below ML
PFNA	8.0E-05	4.8E-06	mg/kg	2.00E-04	Below ML	Below ML
PFHxS	4.1E-04	2.6E-05	mg/kg	2.00E-04	Above ML	Below ML
PFBS	1.8E-03	1.2E-04	mg/kg	2.00E-04	Above ML	Below ML
HFPO-DA	1.0E-04	7.2E-06	mg/kg	8.00E-04	Below ML	Below ML

^a Values are for solid matrices from Table 6 EPA Method 1633 draft 3 (December 2022).

^b Minimum level of quantitation (MLs) - The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte.
mg/kg - milligrams per kilogram

where $C18_{Rt}$ is C18 retention time in minutes in a liquid chromatography system; K_{ia} is in m^{-1} (Schaefer et al., 2019).

4. Table 1 shows a comparison table of the soil cleanup levels listed in Table 5 and the limits of quantification (MLs) described in the EPA draft 1633 method. The cleanup levels for all but PFBS and PFHxS are two orders of magnitude below MLs. These soil cleanup levels should be reconsidered due to achievable reported quantitation levels.
5. The cleanup levels specified in Table 5 do not consider the influence of background levels of PFAS that are ubiquitously present in the environment. For instance, detectable concentrations of PFAS in soils collected at remote locations in North America are generally 1 to 2 nanogram per gram (ng/g) or less (Strynar et al., 2012; Rankin et al., 2016). However, maximum concentrations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) of 30 and 10 ng/g, respectively, have been found in soil samples collected from ambient background areas not in the known vicinity of PFAS sources in United States, China, Japan, Norway, Greece, and Mexico (Strynar et al., 2012). These values are typically below concentrations observed at sites impacted by AFFF (McGuire et al., 2014; Anderson et al., 2016). Most importantly, the likely upper ranges of ambient PFAS in soils is three to four orders of magnitude higher than some of the screening levels estimated by Ecology (e.g., Table 4 values protective of drinking water sources are as low as 0.004 to 0.010 ng/g for PFOA and PFOS). Thus, it is unlikely to find soils anywhere in the state of Washington that are lower than some of these values simply because of the non-point deposition of PFAS to soils that affect all areas of North America. Having a quantitative understanding of PFAS background is critical for assessing PFAS at a site of interest and for establishing cleaning up levels. Therefore, background PFAS levels should be established, and these considerations should be included in Ecology's document.

Table 2. Comparison of default SL for soil leaching of PFAS to potable groundwater listed in Table A-3b to EPA method 1633 draft 3 minimum levels of quantitation.

PFAS	Vadose zone	Saturated zone	Units	1633 ^a ML ^b (mg/kg)	Vadose zone	Saturated zone
PFOA	6.3E-05	4.0E-06	mg/kg	2.00E-04	Below ML	Below ML
PFOS	1.7E-04	9.9E-06	mg/kg	2.00E-04	Below ML	Below ML
PFNA	1.2E-05 ^c	7.5E-06 ^c	mg/kg	2.00E-04	Below ML	Below ML
PFHxS	4.4E-04 ^c	2.8E-05 ^c	mg/kg	2.00E-04	Above ML	Below ML
PFBS	6.8E-03 ^c	4.5E-04 ^c	mg/kg	2.00E-04	Above ML	Above ML
HFPO-DA	1.0E-04	7.2E-06	mg/kg	8.00E-04	Below ML	Below ML

^a Values are for solid matrices from Table 6 EPA Method 1633 draft 3 (December 2022).

^b MLs of quantitation - The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte.

^c Values that do not match with Table 5.

Subsection 3.2.5 Soil Cleanup Levels (Screening Levels), Appendix A

The following comments are in reference to the default screening levels (SL) for soil leaching of PFAS to potable groundwater, listed in Table A-3b and estimated using MTCA equation 747-1.

The default SLs for soil leaching of PFAS to potable groundwater, shown in Table 2, are overly conservative when compared to the percentage of PFAS leaching from the soil. A 2023 study (Schaefer et al., 2023) demonstrated that for all PFAAs tested, the fractional decrease in porewater concentration exceeded the fractional decrease in mass removal from the soil. For instance, PFOS porewater concentrations decreased by 76% compared to only a 7.4% decrease in overall PFOS mass removed from the unsaturated zone (Schaefer et al., 2023). The general conclusion was that PFAS with six or more fluorinated carbons would desorb more slowly from soils and have less of an impact on soil pore water compared to shorter-chain PFAS. This suggests that less stringent soil cleanup criteria than the presented in Table A-3B (which considers an equivalent relationship between mass removal and mass discharge) should be used.

In addition, most of the values listed in Table 2 are below the ML values of the EPA method 1633 draft 3, which makes these values non-quantifiable.

Finally, Table A-3 in the guidance document mentions that MTCA Eq. 747-1 was used to determine the SL values. The same equation was used to determine the preliminary MTCA cleanup levels (Table 5). If the latter is true, the values in Table 5 and Table A-3 should match, but only PFOS and PFOA values are the same between the two tables.

We understand that screening values should be higher than the cleanup values. Please, clarify how the screening values were calculated. If the values were calculated with the stated criteria (MTCA Eq. 747-1), the screening and cleanup values should match, which is only the case for PFOS and PFOA.

CHAPTER 4. Sampling for PFAS

Subsection 4.1.1: Assemble Complete PFAS Analyte List, page 28

It may be valuable to establish a plan to take precursor PFAS into account as they may transform into terminal PFAAs (such as PFOA) and artificially inflate concentrations or create sustained concentrations over time.

Section 4.2: Approved Methods and Compound List for Drinking Water

In this section, Ecology recommends the use of EPA methods 537 and 533 for the analysis of PFAS in drinking water.

Please clarify if Ecology expects analysis for all possible PFAS that can be detected with each method, or only the PFAS specified in the current cleanup criteria (six PFAS)? This is important since the analysis of additional PFAS may affect the detection limits depending on the concentration levels.

Please clarify Ecology's plans for other PFAS in the recommended analytical methods, other than the six for which there are proposed screening levels. Will results for all PFAS analyzed be required to be submitted to Ecology? Could these results be used to improve/establish SALs for other PFAS in the future?

Subsection 4.3.2: Non-Specific Test Methods

This section would benefit from more discussion of the uncertainties related to the Total Oxidizable Precursors (TOP) assay and how resulting data are best applied; specifically, since the TOP assay results in the aggressive chemical oxidation of PFAA precursors to stable PFCAs such as PFOA. This transformation process may not occur under environmental conditions, and data generated from TOP assays should not be directly compared to cleanup levels given the current high level of uncertainty regarding if and how quickly these processes may occur at sites.

CHAPTER 5 and Appendix B, Ecological Receptors: Concentrations Protective of Surface Water and Upland Soil

Ecology's development of toxicological benchmarks for PFAS should be detailed further. The information provided currently is not sufficient to justify the Ecology's process for selection of benchmarks. In some cases, there are technical challenges and potential errors with the selected benchmarks. Additional information behind Ecology's process would promote confidence and application of this information for decision-making purposes at PFAS sites.

For example, the selection of the No Observed Effect Concentration (NOEC) (8.28 micrograms per liter [$\mu\text{g/L}$]) for PFOA exposure to zebrafish (Jantzen et al., 2016) is unclear and may be overly conservative. From review of the study upon which it is based, Jantzen et al. (2016) noted that the 828 $\mu\text{g/L}$ PFOA exposure (the highest exposure evaluated in the study) resulted in a 2% statistically significant adverse effect on the growth (length) of zebrafish exposed to PFOA. Biologically, a 2% level of adverse effect is generally considered trivial when deriving ecotoxicological benchmarks (often, effect sizes of 10%, 20%, or 50% are considered). Thus, the 828 $\mu\text{g/L}$ PFOA could be considered a no-effect, safe level of PFOA exposure. There is no need to use the next lowest concentration in the study (8.28 $\mu\text{g/L}$) as the basis for protection.

It also appears that No Observed Adverse Effect Concentrations (NOAECs) or protective values that are below Low Observed Adverse Effect Concentrations (LOAECs) were applied for aquatic life, but LOAECs were applied for wildlife TRVs. This seems inconsistent. It may be more appropriate to target a threshold $\leq 20\%$ effect (e.g., EC20), as these reflect a dose-response relationship and would provide more consistency in the cleanup level basis.

There may be additional instances in which a potentially questionable benchmark value has been selected by Ecology. Ecology should provide more detail on its benchmark derivation process (for all ecological endpoints) and specifically detail the effects and quantitative level of effects observed. Most importantly, Ecology should explicitly note which levels of effect it considers as meaningful points of departure for the regulation of potential adverse risks.

Additionally, the Plant bioaccumulation “KPlant” and earthworm bioaccumulation factor (BAF) values should be detailed further. Specifically, some of these values may be based on measurements of PFAS in tissue on a wet-weight basis and some may be on a dry-weight basis. Presenting the units for the KPlant and BAF values would be helpful, noting if they are on a wet or dry weight basis, and providing more details on the studies from which they were derived. Application of the KPlant and BAF values in models, if used inappropriately, could result in mathematical errors on a factor of as high as 5 to 10. Please be transparent with these calculations and provide more information.

CHAPTER 6. Treatment Technologies

Section 6.1: Liquid Treatment Technologies

Multiple treatment technologies for PFAS in solid and liquid matrices are presented in the draft document. All the liquid treatment technologies are sorption technologies that generate a concentrated matrix requiring disposal, which may constitute an additional challenge for remediation efforts.

We suggest including the implications and challenges for use of sorptive technologies in terms of concentrated waste generation and/or the next steps/options available for the disposal of waste containing PFAS generated from a treatment technology.

Subsection 6.2.3: Thermal Treatment

Although thermal treatment is included as an option, the ability of thermal treatment technologies to fully degrade PFAS is not fully understood, especially when it comes to mass balance. The pros and cons of thermal treatment options (and other options) should be mentioned in this section so that implications are considered when selecting treatment technologies.

Subsection 6.2.4: Soil Washing

The effectiveness of soil washing for removal of PFAS is still being researched. Removal of PFAS depends on the PFAS of interest, with shorter chain PFAS ($C < 6$) more readily removed while longer chain PFAS exhibit rate-limited, nonideal desorption. Soil type and time since the last PFAS exposure can also significantly influence PFAS removal efficiencies and rates (Minh Hong Nguyen et al., 2022). These complications should be mentioned in this section.

General Comment: Off-site Disposal Alternatives for Waste Generated from the Operation of Selected Field-Tested Treatment Technologies

Various treatment technologies for both liquid and solid matrices require additional treatment or disposal. For instance, spent activated carbon, spent ion exchange resins containing PFAS, or contaminated soil recovered from the excavation require off-site disposal. The current draft guidance should include information regarding PFAS waste management strategies or off-site management options. This is a primary concern that should be addressed or referred to in this document so that facilities implementing treatment technologies know how to proceed when PFAS-containing waste is generated.

General Comment: Disposal Criteria for Investigation Derived Waste (IDW)

The criteria for disposal of IDW is missing in the document and should be added, either in Chapter 6 or as an additional chapter/appendix. A section pertaining to IDW is critical as it constitutes a fundamental part of any investigation and/or cleanup operation.

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