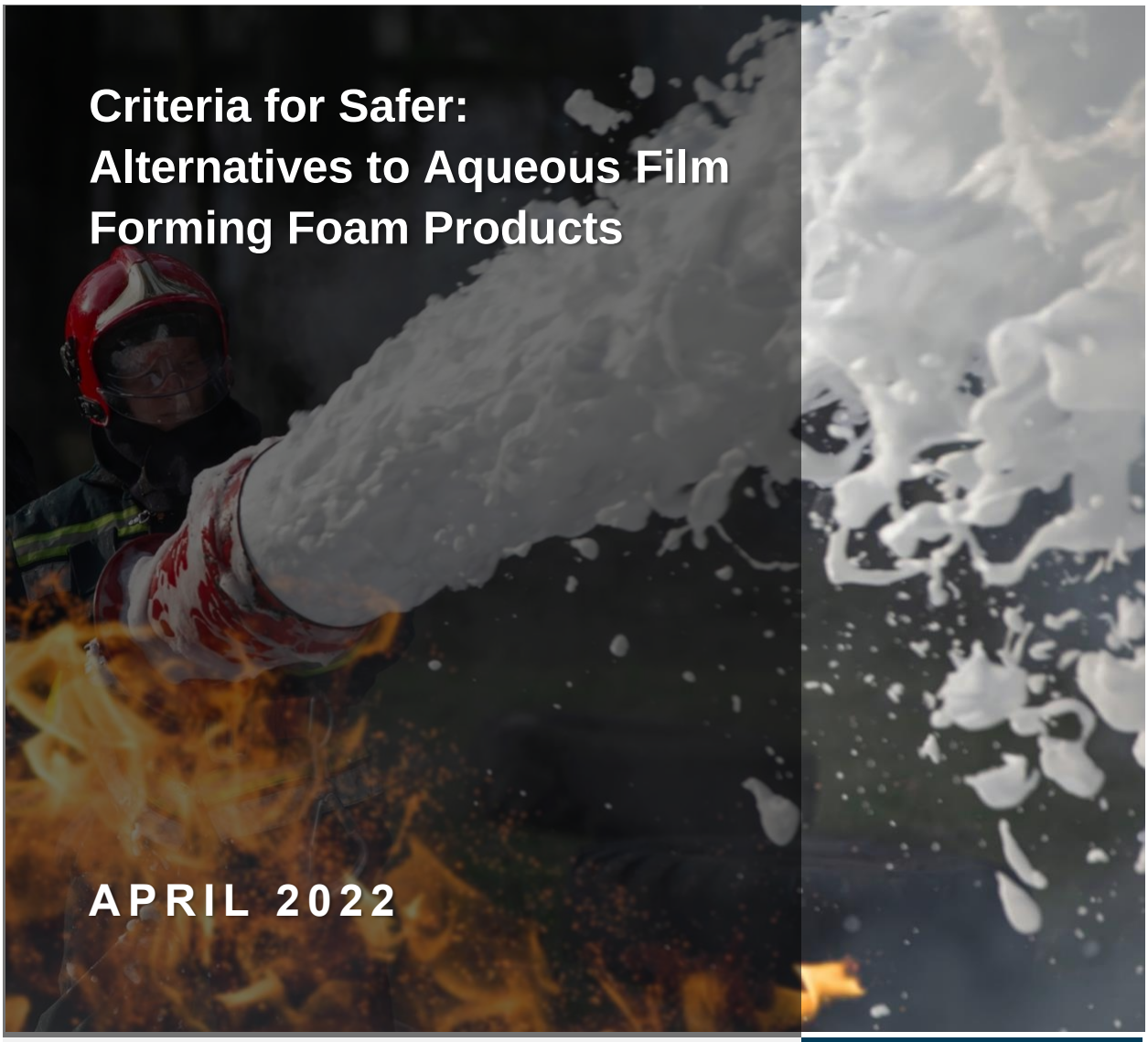
University of Massachusetts Lowell

Criteria for Safer: Alternatives to Aqueous Film Forming Foam Products



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Sustainable Chemistry Catalyst

AUTHORS

Molly Jacobs and Joel Tickner, Sustainable Chemistry Catalyst

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ABOUT

The Sustainable Chemistry Catalyst is an independent research and strategy initiative, based at the Lowell Center for Sustainable Production (University of Massachusetts Lowell), that is focused on accelerating the transition to safer, more sustainable chemistry through research and analysis, and stakeholder engagement with scientists, policymakers, and commercial actors.

The Catalyst works to understand barriers and opportunities to commercialization of safe and sustainable chemistry, identifies model solutions and strategies, develops methods to evaluate safer alternatives, and builds a community of expertise to support the transition to safer, more sustainable chemistries and technologies.

Sustainable Chemistry Catalyst

University of Massachusetts Lowell
Lowell Center for Sustainable Production
61 Wilder St., O'Leary 540
Lowell, MA 01854
(978) 934-2997

www.uml.edu | www.sustainableproduction.org

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ACRONYMS USED

AFFF	Aqueous Film Forming Foam
CAS	Chemical Abstract Service
CIC	Combustion Ion Chromatography
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
DfE	Design for the Environment
ECHA	European Chemicals Agency
EU	European Union
GHS	Globally Harmonized System for the Classification and Labelling of Chemicals
K_{ow}	Octanol-Water partition coefficient
MILSPEC	Military Performance Specification MIL-PRF-24385F(SH)
NAMs	New Approach Methodologies
NDA	Non-Disclosure Agreement
NDAA	National Defense Authorization Act
NGO	Non-governmental organization
NP	Nonylphenol
NPE	Nonylphenol Ethoxylates
OECD	Organization for Economic Cooperation and Development
REACH	Registration, Evaluation and Authorization of Chemicals
PBT	Persistent, Bioaccumulative, and Toxic
PFAS	Per- and polyfluorinated alkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
ppm	Parts per million
SVHC	Substances of Very High Concern
TOF	Total Organic Fluorine
US	United States
US DoD	United States Department of Defense
US EPA	United States Environmental Protection Agency
vPvB	Very Persistent and Very Bioaccumulative

SUMMARY

Policies in the United States (US) and beyond are driving efforts to phase out the use of Aqueous Film Forming Foam (AFFF) products used to extinguish flammable liquid fires at airports, military complexes, oil and gas operations, industrial facilities, and municipal firefighting operations. AFFF contains per- and polyfluorinated alkyl substances (PFAS), which are highly persistent, bioaccumulative and toxic (PBT) substances. This guidance outlines specific criteria to evaluate and determine whether alternatives are safer as compared to current PFAS-containing AFFF products. The criteria should be considered the *minimum requirements* for a safer AFFF alternative determination. Criteria are drawn from existing approaches, in particular the Organization for Economic Cooperation and Development's (OECD) "Guidance on Key Considerations for the Identification and Selection of Safer Alternatives" and supplemented by others such as the Green Screen Certified™ for Fire Fighting Foam and the US Environmental Protection Agency's (US EPA) Safer Choice criteria. This guidance is not a detailed protocol for conducting a hazard assessment; it assumes that users have the necessary toxicological expertise and practicing knowledge for conducting such assessments. Users should recognize that some state, local, or tribal governments in the United States may have additional requirements that should be considered when choosing safer firefighting foams.

The minimum requirements for a safer AFFF alternative determination include Part A and Part B as displayed below in **Table 1**. Conformance with Part A ensures that problematic groups of substances are not used as ingredients (intentionally added or impurities/residuals) in an alternative formulation for such formulation to be considered "safer". Conformance with Part B includes hazard endpoints and/or associated hazard classifications that cannot be of "high" concern for an alternative AFFF formulation to be considered safer.

TABLE 1: Minimum Requirements for a Safer AFFF Alternative

Part A	**Part B**
A **safer** AFFF alternative cannot include the following classes of substances and/or substances: 1. Fluorinated substances (no PFAS) 2. Alkylphenols and alkylphenol ethoxylates unless test data for endpoints in Part B demonstrate safety 3. Cyclic volatile methyl siloxanes: – octamethylcyclotetrasiloxane (D4) – decamethylcyclopentasiloxane (D5) – dodecamethylcyclohexasiloxane (D6)	A **safer** AFFF alternative cannot contain any chemical ingredient* classified as "high" concern associated with the following hazard endpoints: 1. Carcinogenicity* 2. Germ cell mutagenicity* 3. Reproductive/developmental toxicity* 4. Acute mammalian toxicity 5. Systemic toxicity, repeated dose 6. Endocrine disruption 7. Chronic aquatic toxicity Or either of the following classifications: 8. Persistent, Bioaccumulative, and Toxic (PBT)* 9. very Persistent, very Bioaccumulative (vPvB)* A **safer** AFFF alternative tested at the product-level cannot be classified as "high" concern associated with the following hazard endpoint: • Acute aquatic toxicity

**Release, degradation or breakdown products of the formulated product ingredients cannot be of "high" concern either.*

This guidance details methods and criteria for evaluating the minimum requirements above, including use of authoritative lists for an initial rapid screen of problematic ingredients, applying criteria/thresholds using the Globally Harmonized System (GHS) of Classification and Labelling of Chemicals, and using GreenScreen® criteria for persistence and bioaccumulation to support a PBT or very persistent very bioaccumulative (vPvB) classification based on US EPA criteria and/or the Registration, Evaluation and Authorization of Chemicals (REACH) regulation in the EU. The guidance recognizes that GHS criteria for endocrine disruption are currently unavailable. Although such criteria development are anticipated in the coming years, assessors can defer to authoritative lists to ensure problematic endocrine disrupting substances are avoided. The guidance also outlines specific physicochemical properties for evaluating the exposure potential of formulation ingredients, which is especially important for understanding the need for exposure mitigation strategies if ingredients are deemed of "moderate" concern for specific hazard endpoints of interest. Going beyond the minimum is recommended *wherever and whenever possible* to further reduce the likelihood that an alternative to AFFF will result in unintended consequences to the environment, workers, and the public. As such, the guidance outlines additional hazard endpoints to consider beyond the minimum requirements. Of particular importance is the inclusion and evaluation of skin or respiratory sensitization, mobility, the additional data sources for a more comprehensive evaluation of endocrine disruption and adoption of more stringent assessment criteria for aquatic toxicity and environmental fate.

INTRODUCTION / CONTEXT

Background on Aqueous Film Foaming Foams

Introduced in the 1960s, aqueous film forming foam (AFFF) is a type of class B firefighting foam that is formulated using fluorosurfactants to extinguish flammable liquid fires. It is used for firefighting operations at airports, throughout military complexes, by oil and gas operations, at industrial facilities, and at municipal firefighting operations. Up until the early 2000s, AFFF was manufactured with long-chain per- and polyfluorinated alkyl substances (PFAS), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (ASTSWMO 2015). Because of concerns regarding health and environmental impacts and the extremely persistent, bioaccumulative, and mobile properties of these synthetic chemicals, manufacturers in the United States (US) agreed to a complete phase out of these substances by 2015 under the US Environmental Protection Agency's (US EPA) PFOA Stewardship Program. AFFF was subsequently reformulated with shorter-chain PFAS derivatives (US DoD 2018; ASTSWMO 2015; Peshoria et al. 2020).

A growing body of scientific evidence documents that exposure to PFOA, PFOS, and additional PFAS are associated with a range of health impacts, including changes in liver enzymes, decreased birth weight, increased cholesterol levels, decreased vaccine response in children, and increased risk of kidney and testicular cancer, among other health impacts (ATSDR 2021; Fenton et al. 2021). These health impacts and mounting evidence indicating the likelihood of human and ecosystem exposure from contamination of groundwater and surface waters resulting from the use of AFFF during emergency response or training operations have prompted a number of policy efforts to restrict the use of AFFF. Beginning with Washington state in 2018, approximately 14 states have issued regulations prohibiting the sale and/or use of PFAS for firefighting training purposes (Safer States 2021). In addition, the National Defense Authorization Act (NDAA) of 2020 requires the US Department of Defense (US DoD) to revise its military performance specification (MIL-SPEC; MIL-PRF-24385F(SH)) for AFFF to include PFAS-free foams for shore-based applications by 2023 and to phase out the military's use of AFFF by 2024.

PFAS-free alternatives to AFFF have been in use for nearly a decade at airports in Australia and several European countries (Ross 2019). Municipal fire departments in the US are also switching to PFAS-free alternatives (Dykes 2021). The US DoD has significantly invested in the research, development and testing of PFAS-free alternatives given the need for the military to adopt such products by 2024. This research is being supported by requirements in the FY 2021 for DoD to prioritize research on AFFF alternatives that utilize "green and sustainable chemicals that do not pose a threat to public health or the environment" (NDAA 2021). There is a dual focus in these research programs to ensure the effective performance of the PFAS-free alternatives as well as to ensure that alternatives are not regrettable from an environmental health and safety standpoint.

The existing US DoD performance MIL-SPEC specification for AFFF, includes a minimum set of environmental performance measures to avoid detrimental impacts. These include measuring aquatic toxicity on killifish (*Fundulus herteroclitus*), chemical oxygen demand, and biodegradability. However, these environmental endpoints are insufficient considering standards of practice that have emerged over the last decade to support informed substitution, sustainable product design, and environmentally preferable procurement.

Existing Best Practices for Determining a Safer Alternative

Decisions about whether a chemical is considered sufficiently safe for a particular use are often made through quantitative risk assessments, which can be resource intensive and require a significant amount of exposure data. These assessments generally answer the question of whether an exposure level is sufficiently safe or acceptable and may be conducted in response to policy or market demands.

Over the last three decades, a number of hazard assessment methods, approaches, and tools have emerged to support the use of alternatives assessments in informed substitution and safer product design processes. In an alternatives assessment process as compared to risk assessment, the focus is on comparing the hazards, performance, and cost of alternatives in order to identify options that are safer (i.e., less hazardous) and more feasible (i.e., comparable performance and cost-effective) than the incumbent, with the overall goal of facilitating the informed transition to safer alternatives and minimizing the potential for regrettable substitutes. Many of the more recent hazard assessment methods have evolved from the work of the US EPA's Design for Environment (DfE) program. In 2011, US EPA's DfE Program developed its *Alternatives Assessment Criteria for Hazard Evaluation* as a transparent tool to support a comparative evaluation of chemicals based on their human health and environmental hazards (US EPA 2011). Although several hazard assessment and associated classification schemes are available, those that have been used in the context of evaluating alternatives to chemicals of concern are based on a systematic evaluation of specific environmental and human health criteria (US NRC 2014). The United Nation's Globally Harmonized System (GHS) for the Classification and Labelling of Chemicals provides the underlying methodology to support comparisons across alternatives based on specific hazard levels associated with different environmental and human health criteria.

Alternatives assessment methods most often stop short of dictating specific decision-making criteria about whether an alternative is safer than the incumbent chemical or product to be replaced. Traditionally, decisions are left to those seeking to find substitutes or design new products. However, in 2021, the Organization for Economic Cooperation and Development (OECD) issued guidance that aimed to "advance broader agreement on a general approach and criteria for the selection of safer alternatives, with a focus on chemical substitution" (OECD 2021). The guidance was requested by governments and other stakeholders as a process to more consistently define safer chemicals across jurisdictions. The guidance recognizes that the term "safer" rarely implies "safe". A robust inventory of safe and sustainable chemistries and technologies that are benign to human health is currently unavailable for the vast majority of functions

Box A: Examples of Authoritative Definitions of a "Safer" Alternative

US National Research Council – *A safer alternative represents an option that is less hazardous to humans and the environment than the existing chemical or chemical process* (NRC 2014b).

US Occupational Safety and Health Administration – *A safer alternative is an option that is less hazardous for workers than the existing means of meeting that need* (OSHA 2013).

California Safer Consumer Products regulation (California Code of Regulations 2013, p. 13) – *"Safer alternative" means an alternative that, in comparison with another product or product manufacturing process, has reduced potential adverse impacts and/or potential exposures associated with one or more Candidate Chemicals, Chemicals of Concern, and/or replacement chemicals, whichever is/are applicable* (CCR 2013).

Washington State's Pollution Prevention for Healthy People and Puget Sound Act (aka Safer Products for Washington Act) – *A "safer alternative" means an alternative that is less hazardous to humans or the environment than the existing chemical or chemical process* (WA RCW 2020).

and applications currently being served by substances of concern. As such, the best course of action is to use *less hazardous* or *safer* substances while efforts to speed-up the pace of development and application of safer and sustainable chemistry innovations proceed. The OECD guidance helps provide a structure for evaluating safer (some definitions in Box A, previous page) in support of a number of market and regulatory policies.

The OECD (2021) guidance outlines minimum criteria and recommended assessment practices to support a determination of a safer alternative. The guidance emphasizes that minimum requirements need to be seen as the *baseline* in a broader hierarchy of criteria and assessment practices that may ultimately be needed to provide stakeholders with the confidence that a specific alternative is, indeed, safer. Minimum requirements were determined based on regulatory priorities and hazard criteria where data are generally more available than not. To support more comprehensive approaches, the OECD guidance also outlines criteria and recommended practices for going beyond the minimum where possible (**Figure 1**).

FIGURE 1. Organization for Economic Cooperation and Development's (2021) Spectrum of Safer Criteria for the Selection of Alternatives to Priority Substances

The use of minimum requirements for evaluating and making a determination about safer alternatives has also been adopted by government agencies and NGOs for use in regulatory programs and purchasing, including:

- Phase 3 Working Draft Criteria for Safer outlined by the Safer Products for Washington Program – a regulatory program charged with implementation of the Pollution Prevention for Healthy People and Puget Sound Act (Safer Products for Washington Act) (Safer Products for Washington 2021).
- US EPA's Safer Choice Program – used to certify products that carry the EPA's Safer Choice label (US EPA 2012).
- Green Screen Certified™ for Fire Fighting Foam – Clean Production Action's approach used to certify safer firefighting foam products (CPA 2021).
- Registration, Evaluation, and Authorization of Chemicals (REACH) legislation criteria for defining a Substance of Very High Concern (SVHC) (ECHA 2021).

PURPOSE

This guidance outlines specific criteria to evaluate and determine whether alternatives are safer as compared to current PFAS-containing AFFF products. The criteria should be considered the *minimum requirements* for a safer AFFF alternative determination. Criteria are drawn from existing approaches as reviewed above, in particular the OECD guidance (2021), supplemented

by others such as US EPA Safer Choice (2012) and Green Screen Certified™ for Fire Fighting Foam (CPA 2021) to support a more specific assessment of AFFF alternatives given its use context. Given that data gaps and uncertainty are a perennial barrier when examining an array of human health and ecological endpoints, recommendations for addressing uncertain or absent data in the decision-making process are also outlined, including consideration of evidence associated with New Approach Methodologies (NAMs).

This guidance focuses exclusively on a minimum set of toxicological hazard criteria for making a determination of a safer alternative, based on the use context of current AFFF products. As with AFFF, PFAS-free alternative products will result in exposure to humans (especially fire-fighting/emergency response personal) despite industrial hygiene control measures, and to aquatic and terrestrial species given the direct application in outdoor environments. As such, a few endpoints beyond those considered the minimum requirements in the OECD guidance are included. Physicochemical properties should be evaluated to determine if alternatives result in different exposure pathways or if increased exposure may occur, for example when ingredients that have high vapor pressure could increase concern for inhalation exposure. In addition, different substitutes other than the current array of quasi-drop-in PFAS-free alternatives may confer differences in exposure potential and should be evaluated.

The guidance is not a detailed protocol for conducting a hazard assessment. It assumes that users have a practicing knowledge for conducting hazard assessments and have related toxicological expertise. It outlines a minimum set of hazard and related decision criteria to support a safer determination for an AFFF alternative. For methods to support comprehensive hazard assessments, readers are encouraged to review US EPA's Safer Choice Criteria, Version 2.1 (2012) and the GreenScreen® for Safer Chemicals Hazard Assessment Methods (CPA 2018), both of which utilize GHS standardized hazard classifications and testing methodologies (UNECE 2021). Users should recognize that some state, local, or tribal governments in the US may have additional requirements that should be considered when choosing safer firefighting foams.

MINIMUM REQUIREMENTS–CRITERIA FOR A SAFER DETERMINATION

Table 1 outlines the minimum requirements for a safer AFFF alternative determination. There are two parts to these requirements: Part A focuses on ensuring that potentially problematic classes of substances are not ingredients (intentionally added or impurities/residuals) in a safer alternative formulation. Part B focuses on specific hazard endpoints. Part A is consistent with standards being developed by the US DoD to ensure that alternatives to AFFF are fluorine-free and seeks to avoid additional problematic substances and/or substance classes as supported in the Green Screen Certified™ for Fire Fighting Foam methodology (CPA 2021). Part B is consistent with the OECD guidance minimum criteria for *safer*; data must be available for all listed chemicals and their endpoints as *an absence of data is not demonstration of an absence of* hazard.

Assessing alternative AFFF formulations against the minimum requirements for a *safer* determination will require knowledge of the full list of chemical ingredients, including intentionally added substances and impurities/residuals. Without such knowledge, it is difficult to determine if an alternative is indeed safer. Evaluations will therefore require collaborations with product manufacturers and 3rd-party assessors using non-disclosure agreements (NDAs) or

other mechanisms to protect confidential/proprietary ingredients in the product formulation. Known breakdown products should also be considered for each ingredient. Chemical ingredients that release, degrade to, or form breakdown products that are classified as high concern for carcinogenicity, mutagenicity, reproductive/developmental toxicity, or are persistent, bioaccumulative and toxic (PBT) should not be considered safer. Given that the OECD guidance does not specify *de minimis* concentrations requiring assessment, this guidance adopts criteria used by US EPA's Safer Choice program and requires the assessment of all intentionally added ingredients and impurities/residuals present at 100 ppm.

TABLE 1. Minimum Requirements for a Safer AFFF Alternative

Part A	**Part B**
A *safer* AFFF alternative cannot include the following classes of substances and/or substances: 1. Fluorinated substances (No PFAS) 2. Alkylphenols and alkylphenol ethoxylates unless test data for endpoints in Part B demonstrate safety 3. Cyclic volatile methyl siloxanes: – octamethylcyclotetrasiloxane (D4) – decamethylcyclopentasiloxane (D5) – dodecamethylcyclohexasiloxane (D6)	A *safer* AFFF alternative cannot contain any chemical ingredient* classified as "high" concern associated with the following hazard endpoints: 1. Carcinogenicity* 2. Germ cell mutagenicity* 3. Reproductive/developmental toxicity* 4. Acute mammalian toxicity 5. Systemic toxicity, repeated dose 6. Endocrine disruption 7. Acute aquatic toxicity 8. Chronic aquatic toxicity Or either of the following classifications: 9. Persistent, Bioaccumulative and Toxic (PBT)* 10. very Persistent, very Bioaccumulative (vPvB)* A **safer** AFFF alternative tested at the product-level cannot be classified as "high" concern associated with the following hazard endpoint: • Acute aquatic toxicity

**Release, degradation or breakdown products of the formulated product ingredients cannot be of "high" concern as well.*

Assessment Criteria and Related Methods, Part A

To minimize regrettable substitutions, there is a growing commitment to avoid chemistries where multiple substances within the class have been shown to be hazardous, particularly if sufficient comprehensive hazard information demonstrating safety for human and the environment is not available. Exclusion criteria for three specific substances and/or classes of substances are outlined in Part A of the minimum requirements, including: ensuring that (a) the alternative AFFF product does not include fluorinated substances (i.e., no PFAS); (b) that it does not include the cyclic volatile methyl siloxanes, including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6); and (c) that it does not include alkylphenols and alkylphenol ethoxylates (considered hazardous by some authorities). These specific substances and chemical classes were selected because they could be used as replacements for the PFAS surfactant function in AFFF.

A. Avoiding Fluorinated Substances

Despite having hazard data for only a few dozen of the 9,000+ PFAS, there is a commitment by the US DoD to avoid all PFAS in future firefighting foams because substitutions to date within the class have proven to be problematic.

This guidance was developed prior to the release of the revised Milspec for PFAS-free products, which is expected to also dictate testing methodologies to qualify products as PFAS-free. Until such testing standards and specifications are released, total organic fluorine (TOF) testing methodology using combustion ion chromatography (CIC) to ensure a threshold of 0.0001% fluorine by mass can be used as per the GreenScreen Certified™ Standard for Fire Fighting Foam (CPA 2021). TOF/CIC provides for a quantitative assessment of PFAS compounds that are currently detected by liquid chromatography coupled with tandem mass spectrometry methods. TOF/CIC also detects other fluoroorganic compounds that are not readily determined by tandem mass spectrometry methods and is currently the preferred methodology for determining that a product is "PFAS-free" (Bureau Veritas North America, 2021). However, caution is warranted as its unclear whether these testing technologies can achieve the extremely low level of detection (1ppb) for PFAS which will be required in the updated MILSPEC.

B. Avoiding Alkylphenols and Alkylphenol Ethoxylates

The use, discharge, and biodegradation of alkylphenols and alkylphenol ethoxylates represents an ecological hazard. Nonylphenol, an alkylphenol, is used to manufacture nonylphenol ethoxylates (NPEs) and can also become a degradation product of NPEs. NPEs are used as nonionic surfactants and part of the broader category of surfactants known an alkyphenol ethoxylates. Additional NPs and NPEs include octylphenol and octylphenol ethoxylates, respectively. NPs and NPEs are considered environmentally persistent, can range from toxic to extremely toxic to aquatic organisms, and can exert endocrine disruption effects as they mimic estrogen (Soares et al. 2012; US EPA 2009). They also degrade to more toxic and environmentally persistent compounds (Soares et al. 2012). NPEs often partition to sediment and can accumulate (US EPA 2009).

Agencies, including the European Chemicals Agency, have issued restrictions on the use of these NP/NPE compounds. The GreenScreen Certified™ methodology includes alkylphenols and alkylphenol ethoxylates as a class of chemistries that must not be present in order to meet its product certification requirements (CPA 2021). Additional compounds in this chemical class should be considered hazardous unless test data on the range of hazard endpoints in part B demonstrate otherwise. While the extent to which these compounds are being used in PFAS-free foams is unclear, there is a possibility of their use.

C. Avoiding Cyclic Volatile Methyl Siloxanes D4, D5 and D6

In 2018, an alternatives assessment for AFFF was conducted for the European Chemicals Agency (ECHA) to inform risk management options. Siloxane-based alternatives were excluded from the alternatives that were short-listed for further consideration based on stakeholder concerns regarding the toxicity of these substances (Wood, Ramboll and Cowi, 2018). Siloxanes are of interest in PFAS-free formulations because of the surfactant function they provide. However, there is growing understanding that cyclic volatile methyl siloxanes are hazardous. In 2018, the

EU added three cyclic siloxanes, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), to the Candidate List of Substances of Very High Concern (SVHC) for Authorization under REACH based on evidence of PBT and very persistent, very bioaccumulative (vPvB) properties (ECHA 2019). As outlined in **Table 1**, PFAS-free alternatives cannot be considered safer if ingredients in the product formulation have such hazard characteristics. Chemicals on the EU SVHC Candidate List for Authorization do not meet the minimum criteria for defining a safer alternative and should be screened-out. Although it is beyond the purpose of this document to review the science associated with these cyclic siloxanes, we refer readers to the review as outlined in the EU restriction proposals (ECHA, 2019). The GreenScreen Certified™ methodology also includes cyclic volatile methyl siloxanes as a class of chemistries that must not be present to meet product certification requirements (CPA 2021). Additional compounds in this chemical class should be considered hazardous unless test data on the range of hazard endpoints in Part B demonstrates otherwise.

Assessment Criteria and Related Methods, Part B

Ensuring that AFFF alternatives meet minimum criteria for a safer determination associated with priority human and environmental health hazard endpoints requires: (a) the use of authoritative lists for an initial rapid screening of problematic ingredients; (b) applying criteria/thresholds using GHS criteria; and (c) using criteria developed by US EPA Safer Choice Program and GreenScreen® for aquatic toxicity, persistence, and bioaccumulation.

A. Using Authoritative Lists

Authoritative lists are developed by government agencies or authoritative scientific organizations and used in hazard assessment to screen out unacceptable substances based on demonstrated scientific concern for human health and the environment. These lists are developed based on extensive expert review of the scientific evidence. Use of authoritative lists is an established approach in alternatives assessment to support efficient screening out of alternatives that are deemed "chemicals of concern" and may be a current or future focus of regulatory or market-based actions that restrict use (NRC 2014; OECD 2021). Assessors should cross-reference AFFF ingredients using both chemical names and chemical abstract service (CAS) numbers against a given authoritative list. If a chemical ingredient is on the given authoritative list, the alternative formulation would *not* be considered safer.

A set of 13 authoritative lists are outlined in this document as part of the minimum requirements in support of a safer AFFF alternative determination. These lists are outlined in association with the ten required hazard endpoints noted in **Table 1** and outlined in **Tables 2-11** below. Additional authoritative lists that do not easily fit within an individual hazard endpoint evaluation, but which should be reviewed when considering a safer AFFF alternative, are outlined in **Table 12**. This minimum set of authoritative lists include those created by US, Canadian, and European government authorities and those used in international treaties. All are included in the OECD guidance's minimum criteria (2021) and additional lists have been added given the need to also prioritize aquatic toxicity and acute mammalian toxicity. One additional list is also included to support the assessment of carcinogenicity – the National Institute for Occupational Safety and Health's Occupational Carcinogen List (NIOSH 2021). Numerous services are available to

support quick queries of authoritative lists in hazard assessments. Pharos Project (www.pharosproject.net) is one such service and includes all authoritative lists outlined in the minimum requirements in this document as well as dozens of others. US EPA's Center for Computational Toxicology will soon be releasing its Hazard Comparison Dashboard, which also includes a number of authoritative lists outlined in this guidance.

It is important to note that the primary criteria for endocrine disruption in the assessment of the minimum requirements for a safer alternative determination is based on review of authoritative lists. As of this writing, there are no standardized GHS criteria for the evaluation of endocrine disruption. As such, assessors should use authoritative lists. The main authoritative list that addresses endocrine disrupting chemicals is the EU Candidate List of Substances of Very High Concern (SVHC) for Authorization.

B. Apply Globally Harmonized System (GHS) of Classification and Labelling of Chemicals

Ensuring that an alternative AFFF formulation is safer requires going beyond the use of authoritative lists, as only a small subset of substances have been assessed and reviewed by government authorities for their addition to such lists. GHS provides internationally harmonized and standardized criteria for classifying substances and mixtures according to their human health, physical, and environmental hazards (UNECE 2019). Applying GHS criteria for a specific hazard endpoint allows assessors to review the current scientific evidence and categorize an alternative as Low, Moderate, or High concern for a given hazard. Those considered of "High" concern associated with specific hazard criteria among the minimum requirements should be *removed* from further consideration as a safer alternative.

It is important to note that although safety data sheets including GHS hazard statements, these sources should not be used as the primary means to evaluate the hazard profile of alternatives. SDSs are often incomplete and may not represent an updated understanding of toxicity information for the array of hazard endpoints. In addition, not all ingredients are required to be disclosed in an SDS making understanding of hazards more complicated. Lastly, in the US not all GHS recommended fields are required to be outlined in an SDS – neither ecological information nor disposal information sections are required by the US Occupational Safety and Health Administration.

As stated above, assessing the hazard of alternative AFFF formulations against GHS criteria requires knowledge of the full list of chemical ingredients, including intentionally added substances (present at any % in the concentration) and impurities/residuals (present at more than 100 ppm). Chemical ingredients are assessed against the minimum requirements for each hazard endpoint, with the exception of acute aquatic toxicity where the assessment supports the use of test data at the product level. This guidance adopts GreenScreen Certified™ provision for product-level testing for acute aquatic toxicity given challenges with evaluating surfactants – the vast majority of surfactants demonstrate inherent acute aquatic toxicity at the ingredient level. Using the product-level evaluation allows for considerations such as conditions of use, but should be revisited over time as new methodologies are developed for the evaluation of surfactants

As mentioned above, data must be available and reviewed for the minimum set of hazard endpoints in **Table 1**; *an absence of data is not demonstration of an absence of hazard.* Minimizing

regrettable substitutes requires avoiding the transition towards an alternative for which the hazards are not adequately understood. Sources for hazard data may include the scientific literature, peer reviewed industry data, and government reports and databases. Data may include:

- Measured data on the chemical ingredient following a test guideline
- Measured data on a suitable analog for the chemical ingredient following a test guideline
- Estimated data on the chemical ingredient or suitable analog chemical
- Additional new Approach Methodologies (NAMs), including *in vitro* or *in silico* data to support addressing data gaps and uncertainties

Nearly every assessment examining the hazard profile of chemical ingredients in a product formulation will encounter data uncertainties. Assessors should use their expert judgement to reconcile conflicting studies using a strength of the evidence approach to assign a GHS classification. As stated earlier in this guidance, only those assessors with a practicing knowledge for conducting hazard assessments and related toxicological expertise should undertake such state-of-evidence reviews. Significant investment in the development of NAMs to assess the human and ecological toxicity of chemicals has resulted in validated assays and data repositories to help predict potential hazards, which can be a useful resource to reconcile data uncertainties and data gaps. Appendix A outlines a range of methodologies and data tools for the hazard endpoints/classification that need to be assessed to meet minimum requirements for a safer alternative determination**.** *If any of the key hazard endpoints/classifications cannot be addressed due to significant data gaps or uncertainties, then the product should not be considered a safer alternative.*

GHS does not include criteria for persistence or bioaccumulation. These are crucial given concerns with AFFF. As such, this guidance adopts the standard used by GreenScreen® and includes additional assays beyond the aquatic environment, including soil/sediment and air impacts (CPA 2018). Evaluation of persistence and bioaccumulation should be used for establishing a PBT or vPvB classification per the minimum requirements. See Appendix B for classification criteria based on criteria established by the US EPA and under the REACH regulations in Europe.

Tables 2-11 below outline the authoritative lists, GHS and GreenScreen® criteria, and the associated classifications and/or thresholds for a determination of "high concern" related to the 10 hazard endpoints required for a determination of a *safer* alternative. **Table 12** outlines additional authoritative lists that should be reviewed.

TABLE 2. Authoritative Lists and GHS Criteria to Assess a High Concern for Carcinogenicity

These criteria assess whether a compound is known, presumed, or suspected to increase the incidence of cancer.	
	Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative cannot be considered safer.
High Concern for Carcinogenicity	***Authoritative Lists*** US National Toxicology Program • Known to be a Human Carcinogen • Reasonably Anticipated to be a Human Carcinogen International Agency for Research on Cancer • Group 1 – Carcinogenic to humans • Group 2A – Probably carcinogenic to humans • Group 2B – Possibly carcinogenic to humans NIOSH Occupational Carcinogen List California Proposition 65 List of Chemicals Known to Cause Cancer EU Substances of Very High Concern (SVHC) Candidate List for Authorization EU Substances of Very High Concern (SVHC) Authorization List Harmonized GHS Classifications -- Annex VI of the EU Classification, Labeling and Packaging (CLP) Regulation • Category 1A: Substances known to have carcinogenic potential for humans • Category 1B: Substances presumed to have carcinogenic potential for humans • Category 2: Suspected human carcinogen
	GHS Criteria^* • Category 1A • Category 1B
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021 * Although GHS Category 1A/1B is consistent with a classification of high concern for carcinogenicity across the methodologies used in this report, chemicals classified as GHS Category 2 carcinogens should be used with caution as data from available animal or mechanistic studies support concern for carcinogenicity, but sufficient data from epidemiological studies to verify effects in humans are lacking.	

TABLE 3. Authoritative lists and GHS Criteria to Assess a High Concern for Mutagenicity

These criteria are designed to assess whether a compound is known, presumed, or suspected to cause heritable mutations in the germ cells of humans.	
	Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative **cannot** be considered safer.
High Concern for Mutagenicity	***Authoritative Lists*** EU Substances of Very High Concern (SVHC) Authorization List EU Substances of Very High Concern (SVHC) Candidate List for Authorization Harmonized GHS Classifications -- Annex VI of the EU Classification, Labeling and Packaging (CLP) Regulation • Category 1A: Substances known to induce heritable mutations in the germ cells of humans • Category 1B: Substances to be regarded as if they induce heritable mutations in the germ cells of humans
	GHS Criteria^ • GHS Category 1A • GHS Category 1B
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 4. Authoritative Lists and GHS Criteria to Assess a High Concern for Reproductive and/ or Developmental Toxicity

These criteria are designed to assess whether a compound is known, presumed, or reproductive and/or developmental toxicant. Reproductive toxicity may include alterations to the female or male reproductive organs, the related endocrine system, or pregnancy outcomes. The manifestation of such toxicity may include, but not be limited to, adverse effects on onset of puberty, gamete production and transport, reproductive cycle normality, sexual behavior, fertility, gestation, parturition, lactation, developmental toxicity, premature reproductive senescence, or modifications in other functions that are dependent on the integrity of the reproductive systems. Developmental toxicity includes adverse effects in the developing organism that may result from exposure prior to conception (either parent), during prenatal development, or postnatally to the time of sexual maturation. Adverse developmental effects may be detected at any point in the lifespan of the organism including: (1) death (2) structural abnormality, (3) altered growth, and (4) functional deficiency.	
High Concern for Reproductive and/or Developmental Toxicity	**Exclusion Criteria** If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative **cannot** be considered safer. ***Authoritative Lists*** California Proposition 65 List of Chemicals Known to Cause Cancer or Reproductive Harm EU Substances of Very High Concern (SVHC) Candidate List for Authorization Harmonized GHS Classifications -- Annex VI of the EU Classification, Labeling and Packaging (CLP) Regulation • Category 1A/B: Known to have produced an adverse effect on reproductive ability or capacity or on development in humans; presumed to produce an adverse effect on reproductive ability or capacity or on development in humans. US NIH – Reproductive & Developmental Monographs • Clear evidence of adverse effects – Reproductive ***GHS Criteria^*** • Category 1A/B
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 5. Authoritative Lists to Assess a High Concern for Endocrine Disruption

Given that no GHS criteria are available to assess endocrine disruption at this time, assessors should use authoritative lists.	
High Concern for Endocrine Disruption	**Exclusion Criteria** If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative **cannot** be considered safer. ***Authoritative Lists*** • EU Substances of Very High Concern (SVHC) Candidate List for Authorization • EU Substances of Very High Concern (SVHC) Authorization List

TABLE 6. Authoritative Lists and GHS Criteria to Assess a High Concern for Acute Mammalian Toxicity

These criteria evaluate the acute mammalian toxicity occurring following oral or dermal administration of a single dose of a substance, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours. Animal LD_{50} (oral, dermal) or LC_{50} (inhalation) are used.	
High Concern for Acute Mammalian Toxicity	**Exclusion Criteria** If a substance in an AFFF alternative formulation carries the following GHS classifications, in conjunction with a high classification for persistence (Table 10) or a high classification for bioaccumulation (Table 11),the AFFF alternative **cannot** be considered safer. GHS Criteria^ for any route of exposure (oral, dermal, inhalation (vapor/gas), inhalation (dust/mist/fume), LD/LC_{50}: • Category 1/2 oral, dermal and inhalation. Fatal if swallowed; fatal in contact with skin; fatal if inhaled. • Category 3 dermal and inhalation. Toxic if swallowed; toxic in contact with skin; toxic if inhaled.
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 7. GHS Criteria to Assess a High Concern for Systemic Organ Toxicity (Repeated Dose)

These criteria evaluate mammalian toxicity using repeated doses and different routes of exposure. Such studies yield information regarding toxicity to specific target organs as well as understanding additional features of toxicity, such as delayed responses, cumulative effects and information on the reversibility/irreversibility of the effect among others.	
	Exclusion Criteria If a substance in an AFFF alternative formulation carries the following GHS classifications in conjunction with a high classification for persistence (Table 10) or a high classification for bioaccumulation (Table 11), the AFFF alternative cannot be considered safer.
High Concern for Systemic Organ Toxicity	GHS Criteria^ for any route of exposure (oral, dermal, inhalation (vapor/gas), inhalation (dust/mist/fume). Toxicity thresholds based on 90 day studies (tripled if 28-day studies conducted). • Category 1 oral, dermal and inhalation. Causes damage to organs through prolonged or repeated exposure • Category 2 oral, dermal and inhalation. May cause damage to organs through prolonged or repeated exposure
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 8. Authoritative Lists and GHS Criteria to Assess a High Concern for Acute Aquatic Toxicity

Acute aquatic toxicity refers to the intrinsic ability of a substance to invoke injury to an organism based on short-term aquatic exposures. Tests should be conducted at the product level.	
	Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative cannot be considered safer.
High Concern for Acute Aquatic Toxicity	*Authoritative Lists* Harmonized GHS Classifications -- Annex VI of the EU Classification, Labeling and Packaging (CLP) Regulation • Category 1 [Hazard Statement]: Very toxic to aquatic life • Category 2 [Hazard Statement]: Toxic to aquatic life
	*GHS Criteria^* • Category 1 • Category 2
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 9. Authoritative Lists and GHS Criteria to Assess a High Concern for Chronic Aquatic Toxicity

Chronic aquatic toxicity refers to the intrinsic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which are determined in relation to the life cycle of the organism. Measures of degradability of the substance and bioaccumulation factors are also considered.	
	Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative cannot be considered safer.
High Concern for Chronic Aquatic Toxicity	*Authoritative Lists* Harmonized GHS Classifications -- Annex VI of the EU Classification, Labeling and Packaging (CLP) Regulation • Category 1 [Hazard Statement]: Very toxic to aquatic life with long lasting effects • Category 2 [Hazard Statement]: Toxic to aquatic life with long lasting effects
	*GHS Criteria^* • Category 1 • Category 2
^Use test methods as outlined in UNECE, GHS, Revision 9, 2021	

TABLE 10. Authoritative Lists and GHS Criteria to Assess a High Concern for Persistence for consideration in a PBT or vPvB classification (See Appendix B)

Persistence criteria are based the length of time the chemical can exist in the environment before being degraded or destroyed (i.e., transformed) by natural processes. Degradation as the result of microbial action, hydrolysis, photolysis, and other relevant mechanisms should be considered.	
	Exclusion Criteria If a substance in an AFFF alternative formulation demonstrates the following, the AFFF alternative **cannot** be considered safer in connection with a PBT or vPvB classification.
High Concern for Persistence	*Authoritative Lists* Canadian Environmental Protection Act's Toxic Substances List EU Substances of Very High Concern (SVHC) Authorization List EU Substances of Very High Concern (SVHC) Candidate List for Authorization Stockholm Convention: List of Persistent Organic Pollutants
	*GreenScreen Criteria^* • Soil/sediment: ½ life > 60 days • Water: ½ life > 40 days • Air: ½ life > 2 days
^GreenScreen for Safer Chemicals Hazard Assessment Guidance: Standard for Persistence	

TABLE 11. Authoritative Lists and GHS Criteria to Assess a High Concern for Bioaccumulation for consideration in a PBT or vPvB classification (See Appendix B)

Bioacummulation criteria reflect the capacity for a compound to bioaccumulate as measured by the bioconcentration factor (BCF) and the bioaccumulation factor (BAF).	
	Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists or carries the following GHS classifications, the AFFF alternative **cannot** be considered safer in connection with a PBT or vPvB classification.
High Concern for Bioaccumulation	*Authoritative Lists* Canadian Environmental Protection Act's Toxic Substances List EU Substances of Very High Concern (SVHC) Authorization List EU Substances of Very High Concern (SVHC) Candidate List for Authorization US EPA Persistent Bioaccumulative Toxic (PBT) Chemicals Covered by the TRI Program
	*GreenScreen Criteria^* • Bioaccumulation Factor (BAF): > 1,000 • Bioconcentration Factor (BCF): >1,000 • Log Octanol-Water Coefficient (K_{ow}): >4.5 • Monitoring Evidence: Evidence of the presence in humans or wildlife
^GreenScreen for Safer Chemicals Hazard Assessment Guidance: Standard for Bioaccumulation	

TABLE 12. Additional Authoritative Lists Required to Review (not incorporated into Tables 2-11, but in the OECD Guidance)

Exclusion Criteria If a substance in an AFFF alternative formulation is included on the following authoritative lists, the AFFF alternative **cannot** be considered safer
Montreal Protocol: List of Controlled Ozone-depleting Substances
Canadian Environmental Protection Act's Virtual Elimination List

COMPARATIVE EXPOSURE CONSIDERATIONS

The OECD guidance (2021) includes a section on the conduct of a comparative exposure assessment in conjunction with a hazard assessment to support identifying and selecting a safer alternative. Such an assessment focuses primarily on characterizing "reasonable and foreseeable exposure scenarios" and using physicochemical properties to understand the intrinsic exposure potential of specific substances in the product formulation. The assessment aims to address the question: Is the alternative preferable, equivalent to, or potentially worse than the priority chemical given the potential for exposure? The OECD guidance (2021) states that conducting such an assessment may not be necessary, "if the alternatives have similar forms, use patterns, and physical-chemical properties". In such circumstances, the potential for exposure is expected to be similar to the chemical of concern/product being replaced.

This guidance assumes that the routes of exposure for AFFF alternatives and the intrinsic physicochemical properties of alternatives will be similar to AFFF given similar use conditions and the need for a foam agent/mechanism of action being sought. However, current knowledge of existing PFAS-free alternatives suggests that more product will be needed to fulfill extinguishment requirements in comparison to AFFF. If there is a "high" concern for any of the hazard endpoints/classifications in **Table 1**, Part B, the alternative to AFFF cannot be considered safer, irrespective of exposure potential. If more product is used, the result of the hazard assessment still drives considerations for determinations of being safer.

However, if alternative mechanisms and product types are being pursued to replace the function of AFFF, it will be important to assess whether intrinsic physicochemical properties of the alternatives will change the potential for exposure. For example, if an alternative to AFFF has a significantly lower octanol-water coefficient (log K_{ow}) or higher water solubility compared to the priority chemical, differences in bioavailability should be expected, including increased exposure potential to ecological receptors. This is especially important if for example hazard endpoints in **Table 1** are ranked as "moderate" concern as opposed to of "high" concern. With a "moderate" classification of concern, the alternative is considered "safer", but additional controls to mitigate exposure should be pursued. Understanding the potential for exposure and associated routes of exposure will support such mitigation measures. Additionally, if alternative mechanisms and product types are being pursued resulting in changes in application technologies, potential changes in use and exposure potential should be examined.

Critical physicochemical properties used to estimate and compare the exposure potential for both human and ecological receptors are reviewed by Greggs et al. (2019) and the US National Research Council (2014). **Table 13** (next page) describes these properties with an explanation regarding exposure potential as outlined by the Interstate Chemicals Clearinghouse (2017) and informed by the US National Research Council's (2014) report. Some of these physicochcemical characteristics may be more useful than others in helping to consider the intrinsic exposure potential of alternative AFFF products.

TABLE 13. Physicochemical Properties that Inform Exposure Potential (IC2 2017)

Property	Reason	Guidelines
Volatility/vapor pressure	Volatility/vapor pressure influences how likely the chemical is to be found in the air or how likely it is to enter the body	<10-8 mmHg is considered likely to found in the air; <10-4 mmHg is considered to be more likely to enter the body
Molecular weight	Generally, as molecular weight and size increase, bioavailability decreases (leading to a lower toxicity potential)	>1,000 amu is less likely to be bioavailable
Solubility in water	Generally, a chemical that is highly soluble in water will be more bioavailable, and potentially toxic	
Log Kow	The log of the octanol-water coefficient is an indicator of potential for bioaccumulation, as well as bioavailability	>5 for mammals >4 for aquatic species
Boiling point	The boiling point helps to determine if the chemical will be a liquid or gas at a certain temperature	<25 C will be a gas at room temperature
Melting point	The melting point will determine if the chemical will be a solid or liquid at a certain temperature	<25 C will be a liquid at room temperature
Density/specific gravity	Has implications for where the chemical might partition when with other liquids or gases	
pH	A measure of free hydrogen. Has implications for water solubility and potential damage to cells	For certain products, a pH of >2 and <11.5 is safest for eyes and skin
Corrosivity	Associated with the ability to gradually destroy materials by chemical reaction	GHS criteria used to determine level of concern. Typically, the more extreme the pH (either high or low), the more corrosive the substance will be to the eye, skin, respiratory system, etc.
Environmental partitioning	A measure of how easily molecules or salts will break apart under certain conditions (primarily in solution)	The higher the constant (K_d), the more likely the molecules or salts will break apart
Use characteristics (binding properties) or synergistic effects	Other properties that can help determine the state of the chemical in the environment and biological compartments or interactions with other chemicals found in the environment	The acid dissociation constant (pKa) is used to help identify availability of chemicals to bind to one another. pKas of concern typically range between <3 (acids) and >11 (bases). Synergistic effects identify how other chemicals may impact availability of the chemical of concern. For example, dimethyl sulfoxide (DMSO) easily enters skin. Chemicals dissolved in DMSO can be more biologically available than chemicals dissolved in other solvents

GOING BEYOND MINIMUM REQUIREMENTS

As stated earlier, criteria in this guidance are considered *the minimum requirements for making a safer alternative determination.* Going beyond the minimum is recommended *wherever and whenever possible* to reduce the likelihood that an alternative to AFFF will result in unintended consequences to the environment, workers, and the public more broadly. Where data are available for a broader range of hazard criteria, they should be evaluated and considered. Depending on the context, stakeholders and decision makers may also seek to make additional hazard criteria part of the minimum requirements.

Table 14 outlines hazard criteria that assessors could evaluate to go "beyond the minimum" to support a more comprehensive understanding of hazards associated with an alternative to AFFF. Although a finding of "high concern" related to any one of the hazard endpoints may warrant a decision to still use the alternative, such a finding is important to enhance understanding of risk mitigation measures that need to be implemented while products that are more benign are developed. Going "beyond the minimum" includes a more comprehensive assessment of sustainability metrics as well, such as upstream or downstream chemical or product impacts, resource depletion, circularity, energy use, climate change potential, environmental justice considerations, and worker and community health. Hazard endpoints outlined in **Table 14** are derived from OECD's 2021 guidance. The OECD guidance (2021) also includes a section on broader sustainability metrics that should be considered and added to over time.

TABLE 14. Beyond the Minimum: Additional Hazard Criteria to Consider in Comprehensive Hazard Assessments

Human Health Hazards	Environmental Hazards	Physical Hazards
• Aspiration hazard • Endocrine Disruption • Neurotoxicity • Respiratory and skin sensitization • Serious eye damage/eye irritation • Skin corrosion/irritation	• Mobility • Wildlife toxicity • Eutrophication • Greenhouse gas emissions, ozone depletion, waste generation, and other sustainability endpoints	• Corrosivity • Explosivity • Oxidizing properties • Pyrophoric properties • Self-reactivity • Other physical hazards: aerosols, gases under pressure, organic peroxides, ergonomics, vibration, noise, etc.
OECD 2021: Guidance on Key Considerations for the Identification and Selection of Safer Chemical Alternatives		

Beyond the Minimum for AFFF Substitutes

Priority considerations for an evaluation of AFFF substitutes that go beyond an assessment of minimum requirements for a safer alternative determination, includes consideration of skin or respiratory sensitization, mobility, the additional data sources for a more comprehensive evaluation of endocrine disruption and adoption of more stringent assessment criteria for aquatic toxicity and environmental fate.

Skin and Respiratory Sensitization

Skin and respiratory sensitization are two critical hazard endpoints to consider for AFFF alternatives, especially given a likelihood of both inhalation and dermal exposure to fire and rescue personnel using the product. Once sensitized, very low levels of exposure can induce an

allergic response and some workers will require complete removal from the work setting to control exacerbations of contact dermatitis or asthma – manifestations of allergic sensitization. Data gaps are often prominent for respiratory sensitization, however, as data supporting GHS classifications are limited to direct evidence in humans rather than data derived from animal models.

Mobility

Current efforts are underway to establish criteria for "mobile" substances, particularly those that are considered, "very persistent and very mobile" or "persistent, mobile, and toxic" (Arp et al. 2017; Reemstma et al. 2016). "Mobility" as a hazard criterion reflects intrinsic physicochemical properties that enable substances to easily transport through aquatic systems, including rivers and groundwater and potentially impact drinking water sources. Drinking water treatment processes may not be able to control such substances, which may survive treatment technologies including ozonation and chlorination (Arp et al. 2017). If the same substances have toxic properties, this could lead to serious health consequences. As of this writing, there is a lack of authoritative criteria for "mobility" as connected with persistence as well as with toxic classifications. However, this is a fast-moving topic, and governments, such as those in Europe, are likely to establish such criteria in the near future (Arp et al. 2019). Given that PFAS in AFFF are considered highly mobile substances, this criterion will be important to consider when evaluating substitutes.

Additional Endocrine Disruption Data

Despite being of concern for human health and the environment, the OECD guidance (2021) did not include endocrine disruption as part of the minimum requirements for a safer alternative determination because of the lack of comprehensive testing and data availability on this endpoint and a lack of GHS criteria for standardized assessment purposes. In this guidance, endocrine disruption is considered only in the review of authoritative lists because of the absence of GHS criteria at the time of this writing. However, evaluation of available data on endocrine activity for AFFF alternatives should be pursued wherever possible given increasing scientific and regulatory concern and the fact that the use context will result in an exposure to aquatic ecosystems, including possibly drinking water systems.

Consideration of More Stringent Aquatic Toxicity and Environmental Fate Criteria

AFFF products and their alternatives are applied directly in the environment. As such, they bypass sewage treatment systems which enhance chemical degradation prior to release to sensitive aquatic environments. To go beyond the minimum requirements for aquatic toxicity and environmental fate criteria (bioaccumulation and persistence), assessors should consider using US EPA's Safer Choice criteria for direct release products (US EPA 2021). The Safer Choice Program has tightened its standard beyond those outlined by GHS for acute and chronic aquatic toxicity for direct release products. This standard has also been adopted by GreenScreen Certified™ Standard for Firefighting Foam (CPA 2021) for its gold and platinum-level certifications, given that AFFF products are used in the ambient environment near streams, rivers and oceans.

Consideration of Additional Sustainability Criteria

The minimum requirements do not include additional sustainability criteria that are ultimately critical for that trade-offs associated with a chemical choice are considered in the context of a product's lifecycle. The US DoD Sustainability Analysis Guidance contains sustainability endpoints that are important to consider, including climate change, ecosystem quality, and resource availability (US DoD 2020).

CONCLUSION

Transitioning away from the use of AFFF requires ensuring that alternatives are indeed, safer. Use of the minimum criteria for making a safer alternative determination as outlined in this guidance will support consistency across decision makers with regards to what safer means in practice. As data availability and standards for "safer" evolve, so must the minimum requirements. As such, this guidance should be revisited and enhanced over time to support the use and adoption of inherently safer and more sustainable alternatives to AFFF. The approach used in this guidance, adapting the OECD guidance for the specific case of AFFF, can help support consistent review of alternatives for other chemicals and applications of concern, while supporting the transition to safer alternatives.

REFERENCES

Arp HPH, Brown TN, Berger U, Hale SE. 2017. Ranking REACH registered neutral, ionizable and ionic organic chemicals based on their aquatic persistency and mobility. Environ Sci Process Impacts. 19(7):939-955. doi: 10.1039/c7em00158d.

Arp HPH and Hale SE. 2019. REACH: Improvement of guidance methods for the identification and assessment of PMT/vPvM substances. On behalf of the German Environment Agency. June 28. Accessed September 15, 2021

ATSDR [Agency for Toxic Substances and Disease Registry]. 2021. Toxicological profile for Perfluoroalkyls. Atlanta, GA: US Department of Health and Human Services, Public Health Service. Accessed September 14, 2021.

ASTSWMO [Association of State and Territorial Solid Waste Management Officials]. 2015. Perfluorinated Chemicals (PFCs): Perfluorooctanoic Acid (PFOA) & Perfluorooctane Sulfonate (PFOS): Information Paper. Accessed April 23, 2021.

Bureau Veritas North America. 2021. PFAS Analysis Toolkit: LC/MS/MS, Total Oxidizable Precursors (TOPS) and Total Organic Fluorine (TOF). February. Accessed July 30, 2021.

CCR [California Code of Regulations]. 2013. Title 22, Division 4.5, § 69501.1. Definitions. Accessed July 30, 2021.

CPA [Clean Production Action]. 2018. GreenScreen for Safer Chemicals Hazard Assessment Guidance V 1.4. January. Accessed July 30, 2021.

CPA [Clean Production Action]. 2021. GreenScreen Certified™ Standard for Fire Fighting Foam V 2.1. Accessed July 30, 2021.

Dykes K. 2021. Memo: Order Pursuant to General Statutes § 22a-6: Identification of an alternative fluorine-free firefighting foam. June 30. Accessed September 14, 2021.

ECHA [European Chemicals Agency]. Substances of Very High Concern Identified. Accessed July 30, 2021 *[Note this definition is outlined in Article 57 of the REACH regulation - (EC) No 1907/2006]*

ECHA [European Chemicals Agency]. 2019. Annex XV Restriction Report Proposal for a Restriction: Substance Name(s): Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), Dodecamethylcyclohexasiloxane (D6). January 11. Accessed July 30, 2021.

Greggs W, Burns T, Egeghy P, Embry MR, Fantke P, Gaborek B, Heine L, Jolliet O, Lee C, Muir D, Plotzke K, Rinkevich J, Sunger N, Tanir JY, Whittaker M. 2019. Qualitative approach to comparative exposure in alternatives assessment. Integr Environ Assess Manag. Nov;15(6):880-894. doi: 10.1002/ieam.4070.

Houge, C. 2021. Tight EU regulation of three siloxanes recommended. D4, D5, and D6 are persistent, bioaccumulative, and toxic, European Chemicals Agency says. Chemical and Engineering News. April 15. Accessed July 30, 2021.

Fenton SE, Ducatman A, Boobis A, DeWitt JC, et al. 2021. Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. Environ Toxicol Chem. Mar;40(3):606-630. doi: 10.1002/etc.4890.

IC2 [Interstate Chemicals Clearinghouse] 2017. Alternatives Assessment Guide Version 1.1. Accessed September 15, 2021.

NDAA [National Defense Authorization Act]. 2019. National Defense Authorization Act for Fiscal Year 2020. S. 1790 – 11^{6th} Congress (2019-2020). December 20. Accessed May 20, 2021 at:

NDAA [National Defense Authorization Act]. 2021. National Defense Authorization Act for Fiscal Year 2021. H.R. 6395 – 116th Congress (2019-2020). Jan 1. December 20. Accessed May 20, 2021 at:

National Institute for Occupational Safety and Health. 2021. Occupational Carcinogen List. Accessed July 30, 2021.

OECD [Organization for Economic Cooperation and Development]. 2021. Guidance on Key Considerations for the Identification and Selection of Safer Chemical Alternatives. Series on Risk Management No. 60. Accessed September 14, 2021.

Peshoria S, Nandini D, Tanwar RK, Narang R. 2020. Short-chain and long-chain fluorosurfactants in firefighting foam: a review. *Environ Chem Let.* 18(4):1277. doi:10.1007/s10311-020-01015-8.
RCW [Revised Code of Washington]. 2020. Washington Pollution Prevention for Healthy People and Puget Sound Act. RCW 70A.350.010 [Definitions]. Accessed July 30, 2021.

Reemtsma T, Berger U, Arp HP, Gallard H, Knepper TP, Neumann M, Quintana JB, Voogt P. 2016. Mind the Gap: Persistent and Mobile Organic Compounds-Water Contaminants That Slip Through. Environ Sci Technol. Oct 4;50(19):10308-10315. doi: 10.1021/acs.est.6b03338.

Ross I. 2019. Is the burst of the AFFF bubble a precursor to long term environmental liabilities? International Airport Review. July 29. Accessed September 14, 2021.

Safer Products for Washington. 2021. Safer Products for Washington | Phase 3 Working Draft Criteria for Safer. Washington Department of Ecology. Accessed April 26, 2022.

Safer States. Bill Tracker. Accessed September 14, 2021.

State of Washington, Department of Ecology. Safer Products for Washington | Phase 3 Working Draft Criteria for Safer. Accessed July 30, 2021.

Soares A, Guieysse B, Jefferson B, et al. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. 2008. Environ Int. Oct;34(7):1033-49. doi: 10.1016/j.envint.2008.01.004.

UNECE [United Nations Economic Commission for Europe]. 2021. GHS (Rev.9) (2021). Accessed April 26, 2022.

US DoD [United States Department of Defense], Under Secretary of Defense for Acquisition and Sustainment. 2018. Alternatives to Aqueous Film Forming Foam – Report to Congress. Accessed September 14, 2021.

US DoD [United States Department of Defense]. 2020. Sustainability Analysis Guidance: Integrating Sustainability into Acquisition Using Life Cycle Assessment. Version 7.0. Accessed April 26, 2022.

US EPA [United States Environmental Protection Agency]. 2005. Aquatic Life Ambient Water Quality Criteria - Nonylphenol. Final. EPA-822-R-05-005. Office of Water, Washington, DC. Accessed September 15, 2021.

US EPA [United States Environmental Protection Agency]. 2009. DfE Alternatives Assessment for Nonphenol Ethyoxlates. May. Accessed September 15, 2021.

US EPA [United States Environmental Protection Agency]. 2011. Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation Version 2.0. August. Accessed July 30, 2021.

US EPA [United States Environmental Protection Agency]. 2012. EPA's Safer Choice Program Master Criteria for Safer Ingredients. Office of Pollution Prevention & Toxics. Accessed July 30, 2021.

US EPA United States Environmental Protection Agency]. 2021. Criteria for environmental toxicity and fate for chemicals in direct release products. Accessed July 30, 2021.

US NRC [United States National Research Council]. 2014. A framework to guide selection of chemical alternatives. Washington (DC): National Academies Press. Accessed April 23, 2021.

US NRC [United States National Research Council]. 2014b. A framework to guide selection of chemical alternatives. Washington (DC): National Academies Press. P.13. Accessed April 23, 2021.

US OSHA [United States Occupational Safety and Health Administration]. Transitioning to Safer Chemicals: A Tookit for Employers. Basics of Informed Substitution and Alternatives Assessment. Accessed July 30, 2021.

Wood, Ramboll and Cowi. 2018. The Use of PFAS and Fluorine-Free Alternatives in Fire-Fighting Foams. Report for European Commission and the European Chemicals Agency. June. Accessed July 30, 2021.

APPENDIX A: NAMS FOR EVALUATING HAZARD ENDPOINTS

Carcinogenicity

- QSAR methods such as the US EPA's OncoLogic™ tool to estimate the carcinogenicity potential of a chemical
- The *in vitro* Ames test uses *Salmonella typhimurium* bacteria to identify potential chemical carcinogens, using mutagenicity as an endpoint

Mutagenicity

- OECD TG No. 471: Bacterial Reverse Mutation Test Evaluates to evaluate mutagenicity in bacterial cells
- OECD TG No. 473: *In Vitro* Mammalian Chromosome Aberration Test to evaluate chromosomal effects in either human or rodent cells
- OECD TG No. 476: *In Vitro* Mammalian Cell Gene Mutation Tests using the Hprt and xprt genes to evaluate gene mutations in either human or rodent cells
- OECD TG No. 487: *In Vitro* Mammalian Cell Micronucleus Test to evaluate chromosomal effects in either human or rodent cells
- OECD TG No. 490: *In Vitro* Mammalian Cell Gene Mutation Tests Using the Thymidine Kinase Gene to evaluate gene mutations in either human or rodent cells

Reproductive toxicity

- QSAR methods as described in Basant et al., 2016, *Toxicology Research* (doi: 10.1039/c6tx00083e)

Developmental toxicity

- QSAR methods as described in Marzo et al., 2016, Methods in Molecular Biology (doi: 10.1007/978-1-4939-3609-0_8)

Persistence

- QSAR methods such as the EPI Suite™ KOWWIN™ program to estimate the log octanol-water partition coefficient (log KOW)

Bioaccumulation

- QSAR methods such as the EPI Suite™ BCFBAF™ program to estimate fish bioconcentration factor

Chronic aquatic toxicity

- QSAR methods such as the EPI Suite™ ECOSAR™ program to estimate long-term or delayed aquatic toxicity in fish aquatic invertebrates, and green algae
- US EPA Whole Effluent Toxicity (WET) Method 1000.0: Fathead Minnow, Pimephales promelas, Larval Survival and Growth; Chronic Toxicity Test
- US EPA Whole Effluent Toxicity (WET) Method 1001.0: Fathead Minnow, Pimephales promelas, Larval Survival and Teratogenicity; Chronic Toxicity
- US EPA Whole Effluent Toxicity (WET) Method 1002.0: Daphnid, Ceriodaphnia dubia, Survival and Reproduction Test; Chronic Toxicity
- US EPA Whole Effluent Toxicity (WET) Method 1003.0: Green Alga, Selenastrum capricornutum, Growth Test; Chronic Toxicity

Acute aquatic toxicity

- QSAR methods such as the EPI Suite™ ECOSAR™ program to estimate short-term aquatic toxicity in fish aquatic invertebrates, and green algae
- OECD TG No. 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test to evaluate toxicity to algae

- OECD TG No. 202: *Daphnia sp.* Acute Immobilization test to evaluate toxicity to freshwater invertebrates
- OECD TG No. 211: *Daphnia magna* Reproduction Test to evaluate reproductive effects in freshwater invertebrates
- OECD TG No. 212: Fish, Short-term Toxicity Test on Embryo and Sac-Fry Stages to evaluate toxicity to fish development.
- OECD TG No. 218: Sediment-Water Chironomid Toxicity Using Spiked Sediment to evaluate toxicity to sediment-dwelling invertebrates
- OECD TG No. 219: Sediment-Water Chironomid Toxicity Using Spiked Water to evaluate toxicity to sediment-dwelling invertebrates
- OECD TG No. 221: *Lemna sp.* Growth Inhibition Test to evaluate toxicity to freshwater aquatic plants of the genus *Lemna* (duckweed)
- OECD TG No. 222: Earthworm Reproduction Toxicity Test (*Eisenia fetida/Eisenia andrei*) to evaluate reproductive effects in soil invertebrates
- OECD TG No. 225: Sediment-Water Lumbriculus Toxicity Test Using Spiked Sediment to evaluate toxicity of sediment-associated chemicals endobenthic living organisms
- OECD TG No. 233: Sediment-Water Chironomid Life-Cycle Toxicity Test Using Spiked Water or Spiked Sediment to evaluate chronic toxicity to the life-cycle of sediment-dwelling freshwater dipteran Chironomus species
- OECD TG No. 235: Chironomus sp., Acute Immobilisation test to evaluate acute toxicity (immobilisation) to chironomids
- OECD TG No. 236: Fish Embryo Acute Toxicity (FET) to evaluate toxicity to fish using zebrafish embryos
- OECD TG No. 238: Sediment-Free *Myriophyllum spicatum* Toxicity Test to evaluate toxicity to a submerged, rooted macrophyte species (water milfoil)
- OECD TG No. 239: Water-Sediment *Myriophyllum spicatum* Toxicity Test to evaluate toxicity to a submerged, rooted macrophyte species (water milfoil)
- OECD TG No. 242: *Potamopyrgus antipodarum* Reproduction Test to evaluate reproductive toxicity to the mudsnail
- OECD TG No. 243: *Lymnaea stagnalis* Reproduction Test to evaluate reproductive toxicity to a freshwater snail
- OECD TG No. 319A2: Determination of In Vitro Intrinsic Clearance Using Cryopreserved Rainbow Trout Hepatocytes (RT-HEP) to evaluate the capacity for fish (rainbow trout) to metabolically clear chemical via the liver. This in vitro clearance measurement can be applied to models to predict chemical bioconcentration in fish (BCF). The application is described in the guidance document (see OECD Guidance Document [GD] No. 280 under "Other Useful Information" in Appendix B
- OECD TG No. 319B2: Determination of In Vitro Intrinsic Clearance Using Rainbow Trout Liver S9 Sub-Cellular Fraction (RT-S9) to evaluate the capacity for fish (rainbow trout) to metabolically clear chemical via the liver. This in vitro clearance measurement can be applied to models to predict chemical bioconcentration in fish (BCF). The application is described in the guidance document (see OECD Guidance Document [GD] No. 280 under "Other Useful Information" in Appendix B

APPENDIX B: CRITERIA FOR THE IDENTIFICATION OF PERISTENCE, BIOACCUMULATIVE AND TOXIC SUBSTANCES AND VERY PERSISTENT AND VERY BIOACCUMULATIVE SUBSTANCES

PBT criteria as defined by US EPA (as described in US EPA's PBT Profiler documentation)

Persistence

a) Half-life in water, soil, and sediment >60 days; or
b) Half-life in air > 2 days

Bioaccumulation

a) BCF ≥ 1,000

Toxic

a) High concern: Fish chronic value ChV <0.1mg/L. *Note: when EPA reviews when EPA reviews a chemical for its PBT characteristics, they also consider potential human health effects due to environmental exposure in addition to aquatic toxicity.*

PBT criteria as defined under EU's Registration, Evaluation and Authorization of Chemicals (REACH). Annex XIII

Persistence:

A substance fulfills the persistence criterion (P) in any of the following situations:

a) The degradation half-life in marine water is higher than 60 days
b) The degradation half-life in fresh or estuarine water is higher than 40 days
c) The degradation half-life in marine sediment is higher than 180 days
d) The degradation half-life in fresh or estuarine water sediment is higher than 120 days
e) The degradation half-life in soils higher than 120 days

Bioaccumulation:

A substance fulfills the bioaccumulation (B) when the bioconcentration factor (BCF) in aquatic species is higher than 2,000.

Toxic:

A substance fulfils the toxicity criterion (T) in any of the following situations:

a) The long-term no-observed effect concentration (NOEC) or EC10 for marine or freshwater organisms is less than 0.01 mg/l
b) The substance meets the criteria for a GHS classification as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B), or toxic for reproduction (category 1A)
c) There is other evidence of chronic toxicity, as identified by the substance meeting the criteria for classification: specific target organ toxicity after repeated exposure (category 1 or 2)

vPvB criteria as defined under EU's Registration, Evaluation and Authorization of Chemicals (REACH).

Persistence:

A substance fulfils the 'very persistent' criterion (vP) in any of the following situations:

(a) the degradation half-life in marine, fresh or estuarine water is higher than 60 days
(b) the degradation half-life marine, fresh or estuarine water sediment is higher than 180 days
(c) the degradation half-life n soil is higher than 180 days

Bioaccumulation:

A substance fulfills the bioaccumulation (B) when the bioconcentration factor (BCF) n aquatic species is higher than 5,000.

Sustainable Chemistry Catalyst

University of Massachusetts Lowell
Lowell Center for Sustainable Production
61 Wilder St., O'Leary 540, Lowell, MA 01854