Wolf: Testimony in support of LD1503 and LD1505 Acts relating to restrictions on perfluoroalkyl and polyfluoroalkyl substances in firefighting foam and other products

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Per- and Polyfluorinated Substances in Firefighting Foam

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Rochester Institute of Technology
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http://theic2.org/

About the IC2

The Interstate Chemicals Clearinghouse (IC2) is an association of state, local, and tribal governments that promotes a clean environment, healthy communities, and a vital economy through the development and use of safer chemicals and products. The goals of the IC2 are to:

- Avoid duplication and enhance efficiency and effectiveness of agency initiatives on chemicals through collaboration and coordination
- Build governmental capacity to identify and promote safer chemicals and products
- Ensure that agencies, businesses, and the public have ready access to high quality and authoritative chemicals data, information, and assessment methods

The functions of the IC2 include:

- Supporting health and environmental agencies with development and implementation of programs to promote use of safer chemicals and products
- Supporting the development of alternatives assessment methods and identification of safer alternatives
- Sharing data and information on use, hazard, exposure, and alternatives
- Sharing strategies and outcomes on chemicals prioritization initiatives
- Building the capacity of agencies by sharing materials, strategies, and trainings
- Assisting agencies in meeting the relevant information needs of businesses, consumers, and the public

The IC2 is a program of the Northeast Waste Management Officials' Association (NEWMOA). For more information visit: http://theic2.org.

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Glossary

alternatives assessment: The process for identifying and comparing potential chemical and non-chemical alternatives that could replace chemicals of concern on the basis of their hazards, comparative exposure, performance, and economic viability.[1]

aqueous film-forming foam (AFFF): A synthetic firefighting foam developed for Class B fires consisting of a fluorochemical and hydrocarbon surfactants combined with high boiling point solvents and water. AFFF have low viscosity and spread rapidly across the surface of most hydrocarbon fuels, forming a water film beneath the foam to cool the fuel, smother the fire, and stop the formation of flammable vapors.

C6 foam: Short-chain, fluorinated firefighting foams that contain perfluorocarboxylic acids (PCAs) with carbon chain lengths of seven and lower, which include perfluorohexanoic acid (PFHxA) and perfluorosulfonic acids (PFSAs) with carbon chain lengths of five and lower, as well as perfluorobutanesulfonic acid (PFBS).

C8 foam: Long-chain, fluorinated firefighting foams that contain perfluorocarboxylic acids (PFCAs) with carbon chain lengths of eight and higher, which include perfluorooctanoic acid (PFOA) and perfluorosulfonic acids (PFSAs) with carbon chain lengths of six and higher, as well as perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS).

Class B fires: Any fire involving flammable liquid(s), such as gasoline, solvents, or other fuels, where blanketing and smothering for vapor suppression is needed.

F-34 fuel: Popularly known as “JP-8” or “JP8” (NATO code for "Jet Propellant 8") , F-34 is a jet fuel that is used widely by the U.S. military. It is specified by MIL-DTL-83133 and British Defence Standard 91-87, and is similar to Jet A-1, a commercial aviation fuel, but with the addition of corrosion inhibitor and anti-icing additives.

firefighting foam: A mixture of air, water, and a foam concentrate that fights fires by blanketing burning fuel, smothering the fire, separating flames from the fuel source, cooling the fuel and adjacent surfaces, and suppressing the release of flammable vapors that can mix with air. (See “water additives” entry for more on the use of the term “water additive(s)” in this report.)

fluorine-free foam (F3): A firefighting foam or other water additive that is free of fluorinated surfactants and thereby containing no fluorine. (See “water additives” entry for more on the use of the term “water additive(s)” in this report.)

fluorosurfactant: Synthetic organofluorine chemical compounds that have multiple fluorine atoms and are made up of two parts: a polar hydrophilic head and a highly hydrophobic fluorocarbon tail. As surfactants, they are more effective at lowering the surface tension of water than comparable hydrocarbon surfactants.

fluorotelomer: Fluorocarbon-based oligomers, or telomers, that are synthesized by telomerization. Some fluorotelomers and fluorotelomer-based compounds are a source of environmentally persistent perfluorinated carboxylic acids, such as perfluorooctanoic acid (PFOA).

GreenScreen® for Safer Chemicals: A globally recognized tool that identifies hazardous and safer chemicals through a rigorous benchmarking scoring system. Products and substances can achieve certification through the assessment program, becoming GreenScreen Certified™.

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[1] The Association for the Advancement of Alternatives Assessment uses this definition from the U.S. National Research Council, https://www.saferalternatives.org/about

per- and polyfluoroalkyl substances (PFAS): A group of synthetic chemicals used to make fluoropolymer coatings and products that are resistant to heat, water, and oil. PFAS have been used in a variety of industries since the late 1940s and include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), which have historically been used in aqueous film forming foam (AFFF).

perfluorooctanoic acid (PFOA): A synthetic, fully fluorinated organic acid (where all hydrogens on all carbons have been replaced by fluorines) comprised of chains of eight carbons that is used in a variety of consumer products and in the production of fluoropolymers. The acid is generated as a degradation product of other perfluorinated compounds. Due to strong carbon-fluorine bonds, PFOA remains stable despite metabolic and environmental degradation. PFOA is a member of a large group of perfluoroalkyl substances (PFAS) that are used to make products more resistant to stains, grease, and water. These compounds have been widely found in consumer and industrial products, as well as in food items. Major U.S. manufacturers voluntarily agreed to phase out production of PFOA by the end of 2015.[2]

perfluorooctane sulfonate (PFOS): A synthetic, fully fluorinated organic acid (where all hydrogens on all carbons have been replaced by fluorines) comprised of chains of eight carbons that is used in a variety of consumer products. It occurs as a degradation product of other perfluorinated compounds. Due to strong carbon-fluorine bonds, PFOS remains stable despite metabolic and environmental degradation. PFOS is a member of a large group of perfluoroalkyl substances (PFASs) that are used to make products more resistant to stains, grease, and water. These compounds have been widely found in consumer and industrial products, as well as in food items. In 2002, the only major U.S. manufacturer voluntarily agreed to phase out production of PFOS.[3]

water additives: A liquid—such as foam concentrates, emulsifiers, and hazardous vapor suppression liquids and foaming agents—intended to be added to water for fire control and extinguishment.[4] While the term “water additive(s)” encompasses all types of products (not only foams) intended to be added to water to extinguish fire, the term “firefighting foam” is frequently used in its place. In this report, unless otherwise noted, “firefighting foam,” or simply “foam,” is used synonymously with “water additive(s).”

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[2] U.S. EPA Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA), 2016, https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final-plain.pdf

[3] U.S. EPA Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS), 2016, https://www.epa.gov/sites/production/files/2016-05/documents/pfos_health_advisory_final_508.pdf

[4] NFPA 18 Standard on Wetting Agents

Acronyms

AFFF	aqueous film-forming foam
DoD	U.S. Department of Defense
FAA	U.S. Federal Aviation Administration
F3	Fluorine free foam
IC2	Interstate Chemicals Clearinghouse
ICAO	International Civil Aviation Organization
IMO	International Maritime Organization
ISO	International Organization for Standardization
MIL-SPEC	U.S. Military Specification for firefighting foams, MIL-PRF-23485F(SH)
NFPA	U.S. National Fire Protection Association
NYSP2I	New York State Pollution Prevention Institute
OECD	Organisation for Economic Co-operation and Development
PFAS	per- and polyfluoroalkyl substances
PFC	perfluorinated compound
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
UNEP	United Nations Environment Programme
U.S. EPA	U.S. Environmental Protection Agency

I. Executive Summary

This document summarizes the results of precursory work to assist with scoping an alternatives assessment of the use of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in Class B aqueous film-forming foam (AFFF), also known as "firefighting foam." AFFF are used to fight fuel fires and typically contain per- and polyfluoroalkyl substances (PFAS). They are responsible for many incidents of contamination of groundwater and drinking water. The goal of the project is to a) help define the parameters for performance evaluation of firefighting foams, b) identify foams containing short-chain PFAS and fluorine-free foams, and c) further inform the scope of any future assessment work to develop alternatives to the use of per- and polyfluorinated substances in firefighting foams.

This work was a project of the Interstate Chemicals Clearinghouse (IC2), an association of state, local, and tribal governments that promotes a clean environment, healthy communities, and a vital economy through the development and use of safer chemicals and products. The project team was led by the New York State Pollution Prevention Institute (NYSP2I) and was carried out by a subgroup of the IC2's Alternatives Assessment Workgroup. The project team worked collaboratively and included IC2 members from state agencies, non-governmental organizations (NGOs), and agencies. Working together in this capacity allowed the team to pool resources and information to further the success of the project.

A note on terminology

Water additives are liquids that are intended to be added to water for fire control and extinguishment. Examples include foam concentrates, emulsifiers, and hazardous vapor suppression liquids and foaming agents.

Firefighting foam is a mixture of air, water, and a foam concentrate that fights fires by blanketing burning fuel, smothering the fire, separating flames from the fuel source, cooling the fuel and adjacent surfaces, and suppressing the release of flammable vapors that can mix with air.

Fluorine-free foam is firefighting foam or other water additive free of fluorinated surfactants, therefore containing no fluorine.

While the term "water additive(s)" encompasses all types of products (not only foams) intended to be added to water to extinguish fire, the term "firefighting foam" is frequently used in its place. In this report, unless otherwise noted, "firefighting foam," or simply "foam," is used synonymously with "water additive(s)."

Notable Findings

Performance Specifications. The requirements of seven performance specifications are summarized and compared. These include U.S. MIL-SPEC and international standards, such as ISO and UL 162. The U.S. MIL-SPEC and International Maritime Organization (IMO) standards are the only ones that require PFAS to be included in the foam formulation. U.S. MIL-SPEC is the only standard that limits PFOA and PFOS content.

Current PFAS in firefighting foams restrictions. In January 2018, the Australian state of South Australia became the first government body in the world to ban fluorinated firefighting foams. This followed bans specifically on PFOA and PFOS by Queensland, its neighboring state to the northeast, in 2016 and by the Government of New Zealand in 2006. In the United States, the recent U.S. Federal Aviation Administration (FAA) Reauthorization Act of 2018 will eliminate the requirement that most U.S. airports use fluorinated firefighting foams within three years. Washington is the first U.S. state to pass a law prohibiting the sale of firefighting foams containing fluorinated chemicals. The Washington ban will take effect in 2020—military, FAA-certified airports, petroleum refineries and terminals, and certain chemical plants will all be exempt from it.

Alternative Foams. Over 90 fluorine-free water additives from 22 manufacturers have been identified and tabulated with relevant data, including product and manufacturer name, country, performance specifications met, product application, product description, and the Chemical Abstracts Service (CAS) Registry Number, name, and percent of disclosed ingredients in the product. While this report focuses on fluorine-free foams, 14 manufacturers of AFFF containing short-chain PFAS, also referred to as "C6 foams," have been identified. There are many C6 foams available on the market as most manufacturers no longer offer eight-carbon chain AFFF (known as "C8 foams") because the industry has voluntarily abandoned those.

PFAS Research & Alternatives Assessment Work. A number of organizations are currently involved in researching PFAS, researching and synthesizing fluorine-free foams, and conducting alternatives assessments of products currently available on the market. Highlights include:

- The Organisation for Economic Co-operation and Development (OECD) / United Nations Environment Programme (UNEP) Global Perfluorinated Compound (PFC) Group released their updated New Comprehensive Global Database of PFAS and accompanying methodology report in May 2018. See the report here: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/
- The U.S. Department of Defense's (DoD) Strategic Environmental Research and Development Program and Naval Research Laboratory have active research projects to develop and characterize fluorine-free foams.
- A Petroleum Environmental Research Forum (PERF) research project aims to capture the state of knowledge of the fate, transport, and effects of short-chain, PFAS-based firefighting foams and fluorine-free foams, and to identify limitations of—and data gaps in—the current studies and data sets. A contract for this work was put out for bid in May 2018 and includes an alternatives assessment for fluorine-containing and fluorine-free foams. The project may use GreenScreen® assessments and may use the IC2 Alternatives Assessment (AA) methodology. The current plan is to include foam ingredient chemicals (as delivered) and their final degradates in the chemical hazard assessment.
- Clean Production Action (CPA) is collaborating with Toxic-Free Future and King County Local Hazardous Waste Management Program to reduce exposure to PFAS in firefighting foam in the State of Washington. The goals are to ensure PFAS-free products are safer and not regrettable substitutes, and to create a list of preferred PFAS-free products using GreenScreen Certified™.

Firefighting Foam Research Findings. Highlights include:

- A number of fluorine-free surfactants have been developed.
- Performance testing of fluorine-free foams is limited and the results of available tests show the performance of fluorine-free foams is not consistent across types.
- The ecotoxicity and impacts on human health of fluorine-free alternatives have not been adequately characterized or assessed. Many contain generic statements that fluorine-free alternatives are preferable because they do not contain fluorine, while some have aquatic and human-health information available on the product safety data sheet.
- Comprehensive papers expand on performance needs for suppressing Class B fires beyond those included in the Core Performance Standards in this report.

Conclusions, Research Needs, and Actions

From the review of firefighting foam performance standards, current and upcoming regulations, identification of fluorine-free foams, other researchers working in this area, and literature, the following conclusions, research needs, and actions have been identified:

1. **Three main information gaps need to be filled to characterize fluorine-free foams in order to promote them as safer alternatives to fluorinated foams:**
    a. **Performance data is uncertain and/or lacking.**
    <u>Research need: Independent testing of fluorine-free foams to validate existing claims and test against others.</u> The U.S. MIL-SPEC and IMO standards are the only performance specifications that require fluorinated surfactants. Performance testing of fluorine-free foams is needed to understand if the performance specifications can be met without the use of fluorinated surfactants. Some fluorine-free foams identified in this report indicate they meet performance specifications. There is some doubt in the firefighting foam industry that fluorine-free foams do in fact meet the standards. Independent performance testing to validate these claims would be beneficial. If foams cannot meet the specification, the testing process will identify exactly what parameter(s) is not being met. Performance testing fluorine-free foams is critical, as the FAA's Reauthorization Act of 2018 no longer requires major FAA airports to use fluorinated foams.
    b. **The makeup of foams is incomplete as many ingredients are protected as confidential business information. Many researchers and those in the firefighting foam industries have raised a concern about whether foams are truly fluorine-free or not.**
    <u>Research need: Identify all fluorine-free foam ingredients and verify they are truly fluorine-free.</u> Ingredients lists present on the safety data sheets of the fluorine-free foams identified in this study were reviewed. Many foams have incomplete lists, as ingredients are deemed confidential business information and excluded. Listing proprietary ingredients makes it impossible to characterize the fluorine-free alternatives to ensure promoted alternatives do not result in regrettable substitution, where one hazardous or toxic ingredient (in this case, fluorinated surfactants) is replaced with another ingredient possessing different hazard characteristics. There is some doubt within the firefighting foam industry that fluorine-free foams are truly free of fluorine. Analyzing a subset of foams would shed light on this concern and help to understand if the foams are completely free of fluorine or if they contain trace amounts.
    <u>Research need: Achieve transparency of ingredients through credible third-party evaluation.</u> Manufacturers may be amenable to an independent, third party evaluating confidential ingredients and formulations in order to report any hazard information without releasing proprietary ingredients and product formulations. This allows users to make informed decisions without releasing confidential business information.
    c. **The ecotoxicity and impacts on human health of most fluorine-free foams and their ingredients have not been characterized or assessed.**
    <u>Research need: Characterize ecotoxicity and human-health impacts of fluorine-free foams, ingredients, and degradation products through third-party hazard and exposure evaluations.</u> Most fluorine-free foams have generic statements that fluorine-free alternatives are preferable because they do not contain fluorine. Some of the fluorine-free foams identified in this report have aquatic toxicity and human-health information available on their safety data sheet. Safety data sheets could not be obtained for all products. Having complete ingredient lists or formulations disclosed to a third party for analysis is critical to ensure the whole formulation is

assessed. Again, characterizing alternative foams will help to eliminate regrettable substitutions.

2. **The use of performance standards across industries is not well understood and characterized.**
   Research need: Dig deeper into mapping performance specifications to applications. A cursory list of industries and situations to which each performance standard applies is included in this report. Reaching out to industry stakeholders, firefighters, and foam manufacturers to validate and expand this list would help to build an understanding of the performance needs for specific fire situations, which could then be used to determine the appropriate foam type for that need.

3. **It is unclear if gaps or discrepancies exist in the performance needs for extinguishing Class B fires and existing performance specifications.**
   Research need: Compare the performance needs and existing performance specifications. It is unclear if performance standards are too strict, not strict enough, or sufficient in all areas of fire suppression. Comparing the needs to standards, such as MIL-SPEC and UL 162, may identify gaps and discrepancies. Working with users knowledgeable about fire suppression needs, foam manufacturers, performance specification authors, and other stakeholders would ensure specifications are appropriate for all.

4. **Organizations are developing fluorine-free foams, characterizing them, and performing alternatives assessments. Washington is the first U.S. state to ban the sale of fluorinated foams.**
   Action: Monitor work by other organizations. The DoD's research to develop and characterize fluorine-free foams, PERF's alternatives assessment of fluorine-free foams, and CPA's work to develop a list of preferable PFAS-free foams are all notable and currently ongoing. The State of Washington is getting ready to implement their ban on the sale of fluorinated foams in 2020 and is currently working to assess alternatives. Their outcomes may be adopted by others and influence policy and product formulations. The landscape is rapidly changing and there may be other organizations in the near future doing similar work.

5. **There is no regulation preventing the use of fluorine-free foams by non-military users, including firefighting training centers, chemical manufacturers, oil refineries, and others.**
   Action: Assist training centers and other non-military users in switching to fluorine-free alternatives. Firefighting training centers do not have to follow the same performance standards as other users and typically use foams that are not certified to a performance standard. There is no regulatory roadblock for training centers to use fluorine-free foams.

2. Project Goals & Approach

The New York State Department of Environmental Conservation (NYSDEC) and many members of the IC2 Alternatives Assessment Workgroup are concerned about the potential or real impact of the use of fluorinated firefighting foams on human health and the environment. They are interested in promoting less toxic alternatives. This project brought these interested parties together through an IC2 subgroup that worked collaboratively to gather information necessary for scoping future alternatives assessment work.

PFAS is used routinely in firefighting water additives designed for Class B fires, typically referred to as “firefighting foams” or simply “foams.” This project is focused on firefighting water additives designed for Class B fires that are free of long-chain (commonly referred to as C8) fluorosurfactants. Alternatives may include foams containing short-chain (or C6) fluorosurfactants or fluorine-free firefighting water additives.

The performance specifications and requirements for Class B firefighting suppressants are not well understood by the IC2 subgroup. Many state agencies have pulled together their own lists of fluorine-free foams, though a comprehensive worldwide search has not been performed. There is some uncertainty about whether or not fluorine-free foams are able to meet the same performance specifications as fluorinated foams. Therefore, the goals of the project are to

1. understand the performance needs and specifications of firefighting foams and the use of PFAS to meet them;
2. identify and characterize alternatives to long-chain (C8), fluorine-containing firefighting foams, including short-chain (C6), fluorinated foams and fluorine-free foams;
3. and identify agencies and researchers that are focused on the use of alternatives to PFAS in Class B firefighting foams, including short-chain (C6) fluorosurfactants and fluorine-free foams, and gather credible information that can be used in future alternatives assessment work.

This work is a precursor for an alternatives assessment of PFOA and PFOS in firefighting foam. The goal of an alternatives assessment is to replace chemicals of concern in products or processes with inherently safer alternatives, thereby protecting and enhancing human health and the environment. The National Academies of Sciences, Engineering, and Medicine’s *A Framework to Guide Selection of Chemical Alternatives* [5] and the IC2’s *Alternatives Assessment Guide,* [6] provide structured frameworks for completing an alternatives assessment. After the chemical of concern is identified (in this case, per- and polyfluorinated chemicals in firefighting foam), the next steps are scoping and problem formulation followed by identifying potential alternatives. The information gathered in this paper intends to help scope and formulate the problem by understanding the performance needs of firefighting foam. It provides ecotoxicity and human-health information to help determine which lifecycle stages should be included in an assessment. The C6 and fluorine-free firefighting foams identified in this paper serve as the potential alternatives identified in the frameworks. The intent is that this formation will be used by other practitioners to develop a robust alternatives assessment.

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[5] National Academies Press, A Framework to Guide Selection of Chemical Alternatives, 2014, http://nap.edu/18872

[6] Interstate Chemicals Clearinghouse, Alternatives Assessment Guide, Version 1.1, 2017, http://www.theic2.org/article/download-pdf/file_name/IC2_AA_Guide_Version_1.1.pdf

3. History of PFAS in Firefighting Foam

PFAS are a group of synthetic chemicals that have been used in a variety of industries since the 1940s. The most well-known PFAS are PFOA and PFOS, and both were widely used to make carpets, clothing, furniture fabrics, and paper food packaging resistant to water and grease. PFOA and PFOS are very persistent in the environment and the human body and studies have indicated that they can cause reproductive and developmental, liver, kidney, and immunological effects as well as tumors in laboratory animals.[7] While the U.S. Environmental Protection Agency's (EPA) PFOA Stewardship Program successfully eliminated the manufacture of PFOA and PFOS in the United States, PFOA and PFOS are still produced internationally and can be imported.

PFAS chemicals are found in AFFF—a synthetic foam consisting of fluorochemical and hydrocarbon surfactants combined with high-boiling-point solvents and water—that was developed for use on Class B fires (e.g. flammable liquids or gases, such as gasoline or other fuels). Firefighting foam is made up of water, air, and a foam concentrate. The foam concentrate is available off the shelf and is mixed with water and air by firefighters during use. When the ingredients are mixed together, a foam blanket is formed that covers the burning fuel, smothers the fire, separates the flames from the fuel source, cools the fuel and adjacent metal surfaces, and suppresses the release of flammable vapors that can mix with air.[8]

The MIL-SPEC for firefighting foams dictates that fluorinated surfactants must be included in Class B foams. Therefore, a fluorine-free water additive cannot meet the MIL-SPEC performance requirements by definition, as it does not contain fluorinated surfactants. All branches of the U.S. military must use fluorinated firefighting foams on bases located in the United States and abroad. Prior to 2018, the FAA incorporated the military specification, requiring major U.S. airports to use fluorinated firefighting foams onsite. Local municipalities may also use and store AFFF onsite. In the U.S., 75% of all AFFF are used by the military, while the remaining 25% are used by municipal airports, refineries, fuel tank farms, and other industries.[9]

There are approximately 190 sites in 40 U.S. states currently known to be contaminated with PFAS[10] with more testing and analysis underway.[11] Training and emergency responses are major sources of groundwater PFAS contamination on military bases. There are concerns that PFAS-contaminated ground water on military bases may be affecting water quality in the surrounding areas, with the water in and around 126 military installations containing potentially harmful levels of PFAS.[12] The U.S. DoD is

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[7] U.S. EPA, Basic Information on PFAS, https://www.epa.gov/pfas/basic-information-pfas

[8] Chemguard, General Foam Information, https://www.chemguard.com/about-us/documents-library/foam-info/general.htm

[9] FAQs Regarding PFASs Associated with AFFF Use at US Military Sites, August 2017, http://www.dtic.mil/dtic/tr/fulltext/u2/1044126.pdf

[10] Northeastern University, Per- and Polyfluoroalkyl Substances, https://pfasproject.com/pfas-contamination-site-tracker/, accessed October 2018

[11] Michigan (https://www.michigan.gov/pfasresponse/), New Jersey (https://www.nj.gov/dep/dsr/publications/Investigation%20of%20Levels%20of%20Perfluorinated%20Compounds%20in%20New%20Jersey%20Fish,%20Surface%20Water,%20and%20Sediment.pdf), New York (https://www.dec.ny.gov/chemical/108831.html), Washington State (https://www.doh.wa.gov/CommunityandEnvironment/Contaminants/PFAS), and Vermont (http://dec.vermont.gov/sites/dec/files/documents/PFAS%20Sampling%20Report%207.10.18%20FINAL.pdf), and are all actively monitoring for PFAS.

[12] DoD: At least 126 bases report water contaminants linked to cancer, birth defects, April 2018, https://www.militarytimes.com/news/your-military/2018/04/26/dod-126-bases-report-water-contaminants-harmful-to-infant-development-tied-to-cancers/

continuing to investigate the extent of PFAS contamination on military bases and surrounding communities.[13]

Historically, foams contained perfluorinated carbon chains that are eight carbons long (C8 foams). Under the 2015 EPA PFOA Stewardship Program, all U.S. foam manufacturers voluntarily reformulated their foams to contain perfluorinated carbon chains six or fewer carbons long (C6 foams) by the end of 2015. C8 fluorosurfactants are persistent, bioaccumulative, and toxic. While C6 fluorosurfactants are persistent, they are thought to be less bioaccumulative and toxic, even though less is known about these compounds and characteristics vary among the class. The toxicity of many C6 fluorosurfactants remains uncharacterized. There is no scientific consensus to conclude that C6 surfactants are preferable to their C8 counterparts.

A number of manufacturers have formulated firefighting foams to be fluorine free. Many of these alternative foams claim to perform as well as fluorinated ones while being completely free of fluorinated surfactants. To date, no independent testing has been performed to validate these claims of fluorine free.

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[13] US Department of Veterans Affairs, Public Health, PFAS, https://www.publichealth.va.gov/exposures/pfas.asp, accessed October 2018

4. Firefighting-Foam and Water-Additive Performance Specifications

There are a number of performance specifications for firefighting foam with varying requirements. The standards in this section were compiled from internet searches and from those mentioned in foam product technical specifications. The initial list of about thirty standards was divided into two groups: 1) core standards, those that many products meet and many governments require, and 2) other standards, those to which products may conform but are not specifically related to firefighting performance or are difficult to find and not widely used. Comparisons and details of the core standards follow in this section and the other standards are described in "Appendix A: Additional Performance Standards" of this report.[14]

Table 1 below summarizes the core performance standards, including typical application(s), scope, and noteworthy attributes. More details, including specific performance requirements, are included in "Appendix B: Core Performance Standards Details."

Table 1. Summary of Core Film-Forming Foam Performance Standards

Standard	Application(s)	Scope	Noteworthy
Australian Government DEF (AUST) 5706 Guidelines for testing fixed Aqueous Film Forming Foam (AFFF) suppression systems Updated 2018	Australian military	• Offers general guidance in relation to testing, guidance for the commissioning tests, and requirements for storage, collection, treatment, and disposal of AFFF and AFFF wastewater. • These guidelines endorse and supplement the general testing provisions included in NFPA 11 (below).	• Criteria are similar to ISO 7203. • Guidelines endorse and supplement the general testing provisions included in NFPA 11.
European Standard EN 1568 Parts 1-4 Updated 2018 Available for purchase https://www.en-standard.eu/	The general-use standard developed by the European Union to replace the individual standards that each country had possessed.	• Includes foam extinguishment and burnback performance, expansion, and drainage. • Covers concentrate storage, use of sea water, aging and heat stability, and physical properties.	• Concentrates are given performance grades (Grade 1-4) for extinguishing performance and Grades A-D for burnback resistance. Grade 1A is the highest achievable grade. • Approved products are not conformance monitored after accreditation.
ICAO The International Civil Aviation Organization (ICAO) Airport Services Manual Updated 2014	International airports	• Includes foam extinguishment and burnback performance. • Covers concentrate physical properties.	• Manual developed by the aviation industry with a focus on rapid extinguishment. • It is primarily used in airports and developed to minimize potential danger to those on flights.

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[14] A good review of foam, foam types, and specification standards can be found in a white paper from Solberg. This paper is from 2002 and is useful to help understand the lay of the land. Many or all of the specifications likely have since been updated. Dlugogorski, B., Kennedy, E., Schaefer, T., & Vitali, J. (n.d.). *What Properties Matter in Fire-Fighting Foams?* (Solberg). See: http://www.solbergfoam.com/getattachment/3fe1d44d-3b44-4714-89f4-4af37e381b5b/WP-WHAT-PROPERTIES-MATTER-IN-FIRE-FIGHTING-FOAMS.aspx

Standard	Application(s)	Scope	Noteworthy
			• It does not explicitly mention the need for foams to be fluorinated.
IMO International Maritime Organization (IMO) Guidelines for the Performance and Testing Criteria and Surveys of Foam Concentrates for Fixed Fire-Extinguishing Systems Updated 2009	foam concentrates for fixed fire-extinguishing systems onboard tankers and chemical tankers	• Includes foam extinguishment and burnback performance. • Covers concentrate storage, use of sea water, and physical properties.	• Guidelines focus on merchant ships. • They are required by many maritime administrations and classification bodies for foam concentrates to be used on board ships in international waters. It arose as part of the implementation of the SOLAS Convention (Safety of Life at Sea), 174 member states comply with the standard. • Criteria are similar to ISO 7203, largely focus on how to perform the tests, and explicitly calls out aqueous film forming concentrate as having fluorinated surfactants.
ISO 7203 Fire Extinguishing Media (Foam Concentrates) Updated 2011	A general-use standard with respect to foam performance; often required by maritime administrators and classification bodies for use on board ships.	• Includes foam extinguishment and burnback performance, expansion, and drainage. • Covers concentrate storage, use of sea water, aging and heat stability, and physical properties. • Criteria are similar to DEF (AUST) 5706.	• Standard has an international focus. • It was not developed with a singular, specific purpose.
LASTFIRE Hydrocarbon Storage Tanks Updated 2015	Used in general and light industry, it dictates foam concentrate procurement specifications by major international oil companies.	• Includes a "best practices" guide. • Has a focus on how foams will behave and degrade over a long period of time and less with rapid extinguishment.	• Standard was developed by a consortium of oil industry leaders. • Its ratings are based on a scale of 100% effectiveness.
NFPA 11 Standard for Low-, Medium-, and High-Expansion Foam Updated 2016	focus on fire fighting systems and atmospheric tank fires	• Focuses on suppression system components, system types, design, installation requirements, and acceptance. • Includes foam expansion and drainage. • Covers concentrate concentration determination.	• NFPA is a very different style of test. Foam is applied to the fuel surface and it is expected to travel across the fuel. NFPA is focused on the transit time of the foam, making it more ideal for tank fires.

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Standard	Application(s)	Scope	Noteworthy
US MIL-SPEC US Military Specification MIL-PRF-23485F(SH) with Amendment 2, 7 Sept 2017 Updated 2017	Applies to all branches of the U.S. military and has been incorporated into FAA specification for major airports.	• Includes foam extinguishment and burnback performance, expansion, and drainage. • Covers concentrate storage, physical properties, corrosion, environmental impact, and fluorine content.	• Specification has focus on rapid extinguishment. • It was developed with the prevention of weapons discharge aboard U.S. Navy ships as the primary focus. • It was approved for use by all U.S. DoD departments and agencies. • It includes maximum PFOA and PFOS content, and requires foam concentrates to contain fluorocarbon surfactants. • There are eight MIL-SPEC-qualified foams.
UL 162 Standard for Foam Equipment and Liquid Concentrates Updated 2018	tank fires	• Requirements are based on the premise that foam equipment and specified types of foam liquid concentrates with which they are intended to be used are to be investigated for use with each other. • Focus on suppression system foam producing equipment, material compatibility, performance • Includes foam extinguishment and burnback performance. • Covers concentrate storage, physical properties, and concentration.	• Standard evaluates specific combinations of foam concentrates and foam equipment together. • It is a pass/fail test. • UL-listed products are monitored with samples sent to UL every three months for conformance testing.
US FAA The US Federal Aviation Administration Updated 2004	major U.S. airports	• States that AFFF agents must meet the requirements of MIL-PRF-24385F.	• Requires compliance with MIL-SPEC.

5. PFAS in Firefighting Foam Regulatory Overview

There has been significant regulatory activity regarding the use of fluorinated chemicals in firefighting foam over the last year. In January 2018, the Australian state of South Australia became the first government body in the world to ban fluorinated firefighting foams. This followed bans specifically on PFOA and PFOS by Queensland, its neighboring state to the northeast, in 2016 and by the Government of New Zealand in 2006. The U.S. FAA Reauthorization Act of 2018 eliminated the need for the majority of U.S. airports to use firefighting foams containing fluorinated chemicals. The first U.S. state to ban Class B fluorinated firefighting foams is Washington, where the sale of the foams will be prohibited as of July 2020. While the information presented here is up to date at the time of publication, the regulatory climate is changing quickly. The reader is advised that the content of this paper may be outdated by new developments as they occur.

5.1 Australia

South Australia was the first Australian state to ban fluorinated firefighting foams in January 2018. Clause 13A(4) of the Environment Protection (Water Quality) Policy 2015 states: "A person must not supply a firefighting foam product unless the producer's certification of its fluorine content is clearly displayed on a label or document provided with the product.[15]"

South Australia's Environment Protection Authority (EPA) provided guidance that further clarifies the requirement:

> The EPA will consider a certification from the producer to be a statement as follows (either clearly displayed on a label or document provided with the product):
>
> - This firefighting foam product does not contain fluorinated organic compounds.
> - Fluorine or fluorinated substances were not used in the manufacture of this firefighting foam product.
> - Equipment used to manufacture this firefighting foam product was either (a) not previously used to contain or manufacture fluorinated organic compounds; or (b) thoroughly cleaned to prevent residual fluorinated organic compounds from being included as contaminants in this firefighting foam product.[16]

Clause 13A(4) also states that "'prohibited firefighting foam product' means a firefighting foam product that contains a fluorinated organic compound or compounds, but does not include a firefighting foam product that is fluorine free."

The State of Queensland banned the use of PFOA and PFOS in firefighting foam in July 2016. The requirements that the state put into place are outlined in the 2016 publication *Operational Policy: Environmental Management of Firefighting*. It reads:

> 6.2.1 Foams containing PFOS (see Explanatory Notes §3, 3.1, 7.2, 7.4, 9.1) Use of foams that contain the fluorinated organic compound PFOS (perfluoro octane sulphonic acid) as well as its salts or any compound that degrades or converts to PFOS at a concentration of greater than that listed in Table

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[15] South Australia Environmental Protection Authority (2018). *Environment Protection (Water Quality) Amendment Policy 2018, Clause 13A(4)*. Retrieved from https://www.legislation.sa.gov.au/LZ/V/POL/2018/ENVIRONMENT%20PROTECTION%20(WATER%20QUALITY)%20AMENDMENT%20POLICY%202018_30.1.2018%20P%20521/30.1.2018%20P%20521.UN.PDF

[16] Ibid. (2018). *Per- and Poly-fluoroalkyl substances (PFAS)*. Retrieved from https://www.epa.sa.gov.au/environmental_info/perfluorinated-compounds

6.2.2 A in foam concentrate must be withdrawn from service and replaced as soon as possible (taking into account related obligations under the Work Health and Safety Act 2011) and no longer used in any situation where they might be released to the environment, including legacy stocks.

6.2.2 Foams containing PFOA & PFOA precursors to be withdrawn (see EN §3.2, 7.2, 7.4) Firefighting foams that contain PFOA, PFOA precursor compounds or their higher homologues, where the total organic fluorine content equivalent to PFOA and higher homologues exceeds that listed in Table 6.2.2 A in foam concentrate must be withdrawn from service as soon as practicable and any held stocks (and any other related wastes) must be secured pending disposal. These materials are to be managed and disposed of as regulated waste.

Table 6.2.2 A – Fluorinated organic compounds limits in concentrates

Compound(s)	Limit (mg/kg)
PFOS (Perfluoro-octane sulfonic acid) and PFHxS (perfluorohexane sulfonate).	10 (sum)
PFOA (Perfluoro-octanoic acid) and higher homologues, PFOA precursors and higher homologous PFCs as the sum of the total oxidisable precursor assay for C7 to C14 compounds (TOPA C7-C14).	50 (as fluorine)

PFOA precursor compounds and their higher homologues include any compounds that potentially degrade or convert to PFOA, such as 8:2 fluorotelomer derivatives, or the higher homologous perfluoroalkyl carboxylic acids (PFCAs) as well as precursors, such as C7 to C14 carbon-chain or similar fluorotelomer derivatives.

6.2.4 Foams containing short-chain fluorotelomers (see Explanatory Notes §7, 7.1–7.5) Foam containing short-chain fluorotelomers (C6 or shorter perfluorinated moieties) can be used if it is found to be the only viable option, after firefighting effectiveness, short and long-term health, safety and environmental risks and property protection characteristics have all been appropriately considered, however, the following requirements must be met:

- The foam must be C6 purity compliant foam (see Definitions).
- No releases directly to the environment (e.g. to unsealed ground, soakage pits, waterways or uncontrolled drains).
- All releases must be fully contained on site.
- Containment measures such as bunds and ponds must be controlled, impervious and must not allow firewater, wastewater, runoff and other wastes to be released to the environment (e.g. to soils, groundwater, waterways stormwater, etc.).
- All firewater, wastewater, runoff and other wastes must be disposed of as regulated waste to a facility authorised to accept such wastes.

5.2 New Zealand

PFOS and PFOA are banned from firefighting foam in New Zealand. They were excluded from the Firefighting Chemicals Group Standard in 2006, effectively banning their import, manufacture, and use in firefighting foams. For more information, visit New Zealand's Ministry of the Environment at http://www.mfe.govt.nz/land/pfas-and-poly-fluoroalkyl-substances

5.3 U.S. Airports

Current FAA regulations require major U.S. airports to use MIL-SPEC-qualified fluorinated firefighting foams. The FAA outlines in *Title 14, Code of Federal Regulations (CFR)* [Part 139] that, in order to issue airport-operating certificates, an airport must

- serve scheduled and unscheduled air-carrier aircraft with more than 30 seats, or

- serve scheduled air-carrier operations in aircraft with more than nine seats but fewer than 31 seats;

Operators of Part 139 airports must also provide aircraft rescue and firefighting (ARFF) services during air-carrier operations that require a Part 139 certificate. Performance requirements for Aircraft Fire Extinguishing Agents includes the following statement:

> AFFF agents must meet the requirements of Mil-F-24385F. It is important to note that if one vendor's foam is mixed with another vendor's foam in the re-servicing process, there must be compatibility between foams to prevent gelling of the concentrate.

The FAA Reauthorization Act of 2018 will no longer require the use of fluorinated chemicals to meet performance standards.[17] Specifically, the legislation states:

> SEC. 332. AIRPORT RESCUE AND FIREFIGHTING.
>
> (a) Firefighting Foam.—Not later than 3 years after the date of enactment of this Act, the Administrator, using the latest version of National Fire Protection Association 403, "Standard for Aircraft Rescue and Fire-Fighting Services at Airports", and in coordination with the Administrator of the Environmental Protection Agency, aircraft manufacturers and airports, shall not require the use of fluorinated chemicals to meet the performance standards referenced in chapter 6 of AC No: 150/5210–6D and acceptable under 139.319(l) of title 14, Code of Federal Regulations.

5.4 Washington State

Washington is the first U.S. state to ban certain firefighting foams containing perfluorinated compounds. A state law, RCW 70.75A,[18] was passed there in early 2018. Highlights include:

- It prohibits the use of PFAS containing Class B firefighting foam for training purposes starting July 1, 2018;
- It prohibits the manufacture, sale, and distribution of PFAS-containing Class B firefighting foam starting July 1, 2020. Military, FAA-certified airports, petroleum refineries and terminals, and certain chemical plants are all exempt from this requirement.
- Manufacturers and sellers of firefighting personal protective equipment have had to notify purchasers in writing if their products contain PFAS and the reasons for using the chemicals as of July 1, 2018.

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[17] The FAA Reauthorization Act of 2018 [H.R.302] became public law in October 2018. It is available online here: https://www.congress.gov/bill/115th-congress/house-bill/302/

[18] See RCW 70.75A here: http://app.leg.wa.gov/RCW/default.aspx?cite=70.75A&full=true

6. Fluorine-Free Firefighting Water Additives and Short-Chain PFAS Foams

A key purpose of this report is to identify firefighting water additives that do not contain PFOA and PFOS—including products that contain short-chain (C6) PFAS and those that are fluorine free. In the U.S. and Europe, there are firefighting water additives for Class B fires that are free of PFOA and PFOS, including those made with short-chain PFAS currently on the market. While some organizations have identified alternative products or chemistries, there is a need for a comprehensive, up-to-date list to help identify alternatives for specific foam applications. To meet this need, a worldwide search for alternative fluorine-free and C6 products/chemistries was done. The results of this research were then organized in one accessible location. The outcome of this work, a list of available short-chain (C6) foams and fluorine-free foams, is below.[19]

Information on fluorine-free and short-chain (C6) foams was compiled from a number of sources, including:

1. **IC2 Alternatives Assessment Workgroup members**. Many workgroup members had compiled their own lists of fluorine-free foams. Members provided these lists and they were reconciled. Throughout the project duration, workgroup members regularly added to the list of alternatives.
2. **NYSP2I's previous work to identify fluorine-free foams**. In *Supply Chain Assessment of Class B Firefighting Foams for New York State Dept. of Environmental Conservation* (January 2018), NYSP2I identified a number of fluorine-free and C6 foams, as well as foam manufacturers.
3. **Organizations working to develop and research fluorine-free foams**. Many organizations have identified fluorine-free or C6 foams; they are listed in "Research Groups & Agencies involved in Firefighting Foam Work" [Section 7] of this report.
4. **An online search for patents was done to identify fluorine-free firefighting foams and surfactants.** Findings are included in "Firefighting Foam Research" [Section 8] of this report.
5. **Online searches for fluorine-free foam products.**
6. **The U.S. DoD Qualified Products Database** was used to identify products qualified under MIL-PRF-24385. All of the products are short-chain (C6) fluorochemicals, since fluorine is required to meet the MIL-SPEC requirements.[20]

6.1 Fluorine-Free Class B Firefighting Water Additives

Over 90 products from 22 manufacturers have been identified. Pertinent information on the products are tabulated and include product and manufacturer name, country, performance specifications met, product application, product description, and the CAS, name, and percent of disclosed ingredients in the product. The main source of product information was manufacturer websites. Ingredient information is collected from product safety data sheets (SDSs), commonly available on manufacturer websites. Where SDSs were not accessible online, they were requested from the manufacturer. All SDSs found online, made available to NYSP2I staff, and other information, including technical data sheets and/or results of performance tests, were reviewed.

A list of fluorine-free foams is found in Table 2 on the following page. A spreadsheet containing links to product information on manufacturer websites, product application and description, SDSs (where available), and ingredients (where available) is available for download on the IC2 website at http://www.theic2.org.

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[19] The list is also available for download from the IC2's website (http://www.theic2.org).

[20] Access the database here: http://qpldocs.dla.mil/

Table 2. Fluorine-Free Class B Firefighting Water Additives [Note: Product information was collected in August 2018. The main source of product information is manufacturer websites and ingredient information is sourced from product Safety Data Sheets (SDSs). It is recommended that readers confirm product information directly with manufacturers as it may have changed since publication. "Product name" is per the manufacturer and does not necessarily match nomenclature used by chemists.]

Manufacturer	Location	No.	Product Name	Type
3F Company	United Kingdom	1	FREEDOL SF	F3[a]
		2	FREEFOR SF 1	F3
		3	FREEFOR SF 2	F3
		4	HYFEX SF 1	F3, Hi-Ex[b]
		5	HYFEX SF 3	F3, Hi-Ex
		6	HYFEX SF 6	F3, Hi-Ex
Aberdeen Foam (Oil Technics Fire Fighting Products)	Scotland, United Kingdom	7	Aberdeen Foam 1% F3	F3
		8	Aberdeen Foam 1% F3-LF	F3, LT[c]
		9	Aberdeen Foam 3% F3	F3
		10	Aberdeen Foam 3% F3-LF	F3, LT
		11	Aberdeen Foam 6% F3	F3
		12	Aberdeen Foam 2% HI-EX	F3, Hi-Ex
		13	Aberdeen Foam 3x3% AR-F3	F3, AR[d]
		14	Aberdeen Foam 3x6% AR-F3	F3, AR
		15	Aberdeen Foam 1x3% F3	F3, AR
Angus Fire (Angus International: Angus Fire, National Foam and Eau et Feu.)	United Kingdom	16	Expandol (a.k.a. Expandol 1-3)	F3, Hi-Ex
		17	Expandol LT (a.k.a. Expandol 1-3LT)	F3, Hi-Ex, LT
		18	Syndura (6% fluorine-free foam)	F3
		19	HiCombat A	F3
		20	Jetfoam 1%	F3
		21	Jetfoam 3%	F3
		22	Jetfoam 6%	F3
		23	Respondol ATF 3-3%	F3
		24	Respondol ATF 3-6%	F3
Auxquimia (ICL Performance Products)(Phos-Chek Fire Retardant)	Spain	25	Phos-Chek 1% Fluorine free	F3
		26	Phos-Chek 3×6 Fluorine free (a.k.a. UNIPOL-FF 3/6)	F3, AR
		27	H-930 synthetic multiexpansion foam concentrates	F3
		28	SF-60L synthetic multiexpansion foam concentrates	F3
Bio-ex	France	29	BIO FOAM 5	F3
		30	BIO FOAM 15	F3, LT
		31	ECOPOL	F3, Hi-Ex
		32	ECOPOL F3 HC	F3
		33	ECOPOL PREMIUM	F3, AR
		34	ECOPOL A 3%/6%	F3
Buckeye Fire Equipment Company	NC, United States	35	Buckeye High Expansion Foam (BFC-HX) (a.k.a. Hi-Ex 2.2)	F3
Dafo Fomtec AB	Sweden	36	Enviro 3% ICAO	F3
		37	Enviro 3x3 Plus	F3, AR
		38	Enviro 3x3 Ultra	F3, AR
		39	Enviro 3x6 Plus	F3, AR
		40	Enviro 6x6 Plus	F3, AR
		41	Enviro USP	F3
		42	LS xMax	F3
		43	LS aMax	F3

Manufacturer	Location	No.	Product Name	Type
		44	MB -20	F3, LT
		45	P 3%	F3
		46	P 6%	F3
Denko	NY, United States	47	6% AFFF	F3
		48	3% AFFF	F3, LT
		49	1% AFFF	F3, LT
		50	Alcohol AFFF 3%-6% Single or Double Strength	F3, LT, AR
		51	High Expansion Foam, Class A or B	F3, Hi-Ex
Fire Safety Devices Pvt. Ltd.	NY, United States	52	Fluorine-free Foam, 1%, 3%, 6%	F3
Fire Suppression Products	MI, United States	53	FIRE CAP PLUS AR-AFFF 1% x 3%	F3, AR
		54	FIRE CAP PLUS	F3
FireFreeze Worldwide, Inc.	NJ, United States	55	Coldfire	F3
FireRein	Canada	56	Eco-Gel	F3
Genius Group	Germany	57	PyroBubbles	F3
Hazard Control Technologies, Inc.	GA, United States	58	F-500	F3
Orchidee Fire	Belgium	59	Orchidex BlueFoam 1x3	F3
		60	Orchidex BlueFoam 3x3	F3
		61	Orchidex BlueFoam 3x6	F3
		62	Orchidex BlueFoam 6x6	F3
Pyrocool Technologies	VA, United States	63	Pyrocool FEF 0.4% Multiclass Foam Concentrate	F3
R. Nickeson Enterprises	MA, United States	64	Novacool UEF Foam	F3
Sthamer	Germany	65	FOAMOUSSE 3% F-15 #5301	F3
		66	vaPUREx LV 1% F-10 #7141	F3
		67	STHAMEX-SV/HT 1% F-5 #9142	F3, LT
		68	MOUSSOL®–FF 3/6 F-15 #7941	F3, AR
		69	MOUSSOL®–FF 3/6 F-5 #7942	F3, AR
		70	STHAMEX® 2% F6 Multi-purpose detergent foam	F3
		71	STHAMEX® K 1% F-15 #9143	F3
		72	STHAMEX® 3% F6 Multi-purpose detergent foam	F3
The Solberg Company (an Amerex Corporation company)	WI, United States	73	RE-HEALING RF1, 1% FOAM CONCENTRATE	F3
		74	RE-HEALING RF1-AG, 1% FOAM CONCENTRATE	F3
		75	RE-HEALING RF1-S, 1% FOAM CONCENTRATE	F3
		76	RE-HEALING RF3, 3% FOAM CONCENTRATE	F3
		77	RE-HEALING RF3-LV, 3% LOW VISCOSITY FOAM CONCENTRATE	F3, LV
		78	RE-HEALING RF3x3% FREEZE PROTECTED ATC FOAM CONCENTRATE	F3, LT
		79	RE-HEALING RF3x6% ATC FOAM CONCENTRATE	F3
		80	RE-HEALING RF3x6% FREEZE PROTECTED ATC FOAM CONCENTRATE	F3, LT
		81	RE-HEALING RF6, 6% FOAM CONCENTRATE	F3
		82	RE-HEALING RF6, 6% FOAM CONCENTRATE	F3

Manufacturer	Location	No.	Product Name	Type
The Solberg Company (Amerex Corporation)	WI, United States	83	RE-HEALING RF-MB FOAM CONCENTRATE	F3
Verde Environmental, Inc. (Micro Blaze)	TX, United States	84	Micro-Blaze Out	F3
vs FOCUM	Spain	85	Silvara 1 (1%)	F3, LV[e]
		86	Silvara APC 3x3	F3
		87	Silvara APC 3x6	F3
		88	Silvara ZFK (0.5%)	F3
		89	Silvara T3	F3
		90	Silvara APC 1	F3, AR
National Foam	PA, United States	91	Universal Green 3%-3%	F3, AR

[a] F3 = Fluorine-free foam or firefighting wetting agent that is advertised to be free of fluorinated surfactants, and therefore free of fluorine.

[b] Hi-Ex = High-expansion foams that have an expansion ratio greater than or equal to 200. They are used when an enclosed space, such as a basement or hangar, must be quickly filled.

[c] LT = Low-temperature foams, sometimes labeled as “freeze free” or “freeze protected,” that are specifically formulated to be used at lower temperatures.

[d] AR = Alcohol-resistant foams that are used as a conventional AFFF on hydrocarbon fuels. They form an aqueous film on the surface of the hydrocarbon fuel. When used on polar solvents (or water miscible fuels), the polysaccharide polymer forms a tough membrane that separates the foam from the fuel and prevents the destruction of the foam blanket. Fifteen AR foams are especially effective for extinguishing and securing flammable hydrocarbon and polar solvent fires. High-risk facilities, such as refineries, pharmaceutical plants, and process areas, often require AR foams.

[e] LV = Low-viscosity foams that are formulated to be thinner than typical foams, thus flowing at a faster rate during application.

6.2 Fluorine-Free Training Foams

Firefighting foam manufacturers typically formulate one or more products specifically for training purposes. These foams do not typically meet performance specifications, as their use in training does not dictate the same level of performance. Similarly, manufacturers have formulated fluorine-free training foams for use at fire academies and other locations for training purposes. Table 3 contains fluorine-free training foams currently available on the market.

Table 3. Fluorine-Free Training Foams [Note: Product information was collected in August 2018. The main source of product information is manufacturer websites and ingredient information is sourced from product Safety Data Sheets (SDSs). It is recommended that readers confirm product information directly with manufacturers as it may have changed since publication.]

Manufacturer	Country	No.	Product Name	Type
3F Company	United Kingdom	T1	T-FOAM SF 3	F3, T
		T2	T-FOAM SF 6	F3, T
Aberdeen Foam (Oil Technics Firefighting Products)	Scotland, United Kingdom	T3	Aberdeen Foam 1% Training Foam (synthetic)	F3, T
		T4	Aberdeen Foam 3% Training Foam (synthetic)	F3, T
Angus Fire	United Kingdom	T5	TF3/TF6 (3%/6% Training Foam Concentrate	F3, T
		T6	Trainol (3% Fluorine-free Training Foam Concentrate)	F3, T
Auxquimia (ICL Performance Products)(Phos-Chek Fire Retardant)	Spain	T7	Phos-Chek Training Foam 136	F3, T
		T8	Phos-Chek Training Foam EE-3	F3, T
Bio-ex	France	T9	BIO T3 (1-3%)	F3, T
Dafo Fomtec AB	Sweden	T10	Trainer E-lite	F3, T
Fire Services Plus	GA, United States	T11	FireAde Training	F3, T
Sthamer	Germany	T12	TRAINING FOAM-N 1% F-0 #9141	F3, T
The Solberg Company (Amerex Corporation)	WI, United States	T13	RE-HEALING TF, TRAINING FOAM CONCENTRATE	F3, T

6.3 Short-Chain (C6) Foams

Most manufacturers no longer offer long-chain (C8) firefighting foams, as the industry has voluntarily switched over to C6 foams. As a result, the universe of C6 products is vast. The project workgroup focused its efforts on identifying and collecting information on fluorine-free alternatives; the manufacturers in Table 4 are those that offer C6 foams. Please visit each manufacturer's accompanying link to learn about the C6 products they offer.

Table 4. Manufacturers of C6 foams [Note: Product information was collected in August 2018. The main source of product information is manufacturer websites and ingredient information is sourced from product Safety Data Sheets (SDSs). It is recommended that readers confirm product information directly with manufacturers as it may have changed since publication.]

Manufacturer	Country	Link
3F Company	United Kingdom	http://www.3fff.co.uk/index.php/en/chemistry-3f-foams-extinguishers-specialities/smart-foams-industryprotection-3f-england-singapore-morocco-2
Aberdeen Foam (Oil Technics Firefighting Products)	United Kingdom	http://www.firefightingfoam.com/fire-fighting-foam/products-a-z/
Angus Fire (Angus International: Angus Fire, National Foam and Eau et Feu.)	United States / United Kingdom	http://angusfire.com/foam-concentrates/
Auxquimia (ICL Performance Products)	Spain	https://phoschek.com/brand/auxquimia-s-a/
BIOex	United Kingdom	http://www.bio-ex.com/products/types-of-risk/class-b-liquid-fires-hydrocarbons/product/biofilm-fluorosynthetic-afff-foam-concentrate-effective-on-hydrocarbon-fires-9
Buckeye Fire Company	NC, United States	http://www.buckeyefire.com/foam-equipment-concentrates/
Chemguard	WI, United States	http://www.chemguard.com/fire-suppression/catalog/foam-concentrates
Dr. Sthamer	Germany	https://sthamer.com/en/AFFF_foam_concentrate.php
Fire Safety Devices Pvt. Ltd.	India	http://fcfsd.com/fire-fighting-foams.html
FireAde	GA, United States	http://pro.fireade.com/products/fireade-climate-control/
Fomtec (Dafo Fomtec AB)	Sweden	https://www.fomtec.com/foam/category33.html
National Foam	PA, United States	http://nationalfoam.com/foam-concentrates/
Orchidee	Belgium	http://www.orchidee-fire.com/foams/
Solberg	WI, United States	http://www.solbergfoam.com/Foam-Concentrates/ARCTIC-Foam.aspx

7. Research Groups and Agencies Involved in Firefighting Foam Work

This section highlights the activities from the many organizations in the U.S. and abroad that are actively engaged in work in fluorine-free foams for Class B fires. It is recommended that readers follow up directly with the organizations listed as their work progresses and new information emerges. More information on the work of the research groups and agencies can be found in "Appendix E: Research Groups and Agencies Involved in AFFF Work."

7.1 Intergovernmental Organizations

1. The OECD/UNEP Global PFC Group released the updated "New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFAS)" and an accompanying methodology report in May 2018. The group's informational portal serves to facilitate the exchange of information on per- and poly-fluorinated chemicals, focusing specifically on PFAS, in order to support a global transition towards safer alternatives. The portal can be accessed at http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/
2. The Interstate Technology and Regulatory Council (ITRC) has developed a series of fact sheets to summarize the latest science and emerging technologies for remediating PFAS-contaminated sites. The fact sheets are tailored to the needs of state regulatory program personnel who are tasked with making informed and timely decisions regarding PFAS-impacted sites. The content is also useful to consultants and parties responsible for the release of these contaminants, as well as community stakeholders. The fact sheets are available at https://pfas-1.itrcweb.org/fact-sheets/

7.2 Government

3. The U.S. DoD's Strategic Environmental Research and Development Program has active projects under its Environmental Research Programs: Per- and Polyfluoroalkyl Substances (PFASs) subsection. These projects focus on the research and development of fluorine-free AFFF for use by the U.S. military.
4. The U.S. Naval Research Laboratory (NRL) has current projects in fluorine-free foam development and remediation of PFAS-contaminated sites, though details of those projects are not available. A number of presentations and papers have been authored by NRL staff and focus on the performance of fluorine-free foams and the role of surfactants in AFFF.
5. The U.S. Environmental Protection Agency (EPA) has initiated the following:
    i. A request for application (RFA) titled "National Priorities: Per- and Polyfluoroalkyl Substances (PFAS)" closed in June 2018. The RFA solicited applications to generate new information for nationally assessing PFAS fate and transport, exposure, and toxicity.
    ii. On January 21, 2015, EPA proposed a Significant New Use Rule (SNUR) under the Toxic Substances Control Act. It required manufacturers, importers, and processers of PFOA and PFOA-related chemicals (including as part of articles) to notify EPA at least 90 days before starting or resuming new uses of these chemicals in any products. This notification would allow EPA the opportunity to evaluate the new use and, if necessary, take action to prohibit or limit the activity. This SNUR is not currently in effect.
    iii. EPA's New Chemicals Program reviews alternatives for PFOA and related chemicals before they enter the marketplace to identify whether the range of toxicity, fate, and bioaccumulation issues that have caused past concerns with perfluorinated substances may be present. This is done in order to ensure that the new chemicals may not present an unreasonable risk to health or the environment.

   iv. Since 2000, EPA has worked to review substitutes to PFOA, PFOS, and long-chain PFAS. The focus is on whether the reviewed substances have similar properties to PFOA, PFOS, or long-chain PFAS, and to then try and determine if the reviewed compound raises any new concerns.

6. EPA has done a lot of work in characterizing and detecting PFAS, as well as characterizing fate and transport, researching ecological risk, exposure, toxicity research with animals, and research with computational modeling of PFAS.
7. The State of Washington was the first U.S. state to ban certain firefighting foams containing perfluorinated compounds. A new law, RCW 70.75A, prohibits (1) the use of PFAS containing Class B firefighting foam for training purposes as of July 1, 2018, and (2) the manufacture, sale, and distribution of PFAS containing Class B firefighting foam starting on July 1, 2020. Military, FAA-certified airports, petroleum refineries and terminals, and certain chemical plants are all exempt from this requirement.
8. Other U.S. states are actively involved in PFAS work to varying degrees. This list is not comprehensive. New Jersey found PFAS substances in surface water, sediment, and fish tissue in 2018. New York surveyed potential users of firefighting foam in the state to determine which facilities may be using PFOA/PFOS foams in order to target them for potential contamination and response. New York had a collection and disposal program for firefighting foam containing perfluorinated compounds. Vermont has identified a number of potential sources of PFAS water contamination. Michigan has established a PFAS response team to investigate sources and locations of PFAS contamination in the state, take actions to protect drinking water, and keep the public informed.
9. The Australian Government is currently investigating the use of PFAS contamination in and around military bases. An Expert Health Panel for PFAS was established to advise on the potential health impacts associated with PFAS exposure and to identify priority areas for further research in 2018. South Australia was the first Australian state to ban fluorinated foams in 2018.

7.3 Industry

10. The Petroleum Environmental Research Forum (PERF) is a non-profit organization created to provide a stimulus to and a forum for the collection, exchange, and analysis of research information relating to the development of technology for health, environment and safety, waste reduction, and system security in the petroleum industry. In May 2018, a project was contracted with an aim to capture the state of knowledge of the fate, transport, and effects of short-chain PFAS-based AFFFs and fluorine-free firefighting foams in order to identify limitations of and data gaps in the current studies or data sets. The project may use GreenScreen® assessments and may use the IC2 Alternatives Assessment methodology. The current plan is to include foam ingredient chemicals (as delivered) and their final degradates in the chemical hazard assessment.
11. The LASTFIRE (“LAST” stands for “Large Atmospheric Storage Tanks”) Project was initiated to review the risks associated with large-diameter, open-top, floating-roof storage tanks. LASTFIRE has developed their own performance standard (see “Firefighting Foam and Water Additive Performance Specifications” [Section 4] of this report for more info) and holds regular foam industry summits.
12. The Dallas/Fort Worth Fire Training Research Center has presented results on the performance of fluorine-free foams and may be a good resource for performance testing. More information is available here: https://www.dfwairport.com/firetraining/#slide-1[21]

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[21] LASTFIRE’s 2018 International Fire Fighting Foam Summit and Fire Extinguishment Tests were held at Dallas/Fort Worth Airport.

7.4 Independent Organizations

13. Clean Production Action is collaborating closely with Toxic-Free Future and King County Local Hazardous Waste Management Program in the State of Washington to reduce exposure to PFAS in firefighting foam by identifying safer alternatives.

8. Firefighting Foam Research

The following section includes information to assist with identifying chemical alternatives for fluorinated compounds in firefighting foam and to characterize their impact on the environment and human health. Understanding the performance needs for suppressing Class B fires, beyond those included in the Core Performance Standards in "Firefighting Foam and Water Additive Performance Specifications" [Section 4] of this report, is also part of this task.

This research is performed to support a future alternatives assessment of firefighting water additives. *A Framework to Guide Selection of Chemical Alternatives*, a 2014 publication from the National Academies of Sciences, Engineering, and Medicine, was consulted to determine the point in the alternatives assessment process at which the research papers included here are most useful. Summaries of the research papers are included in "Appendix F: Firefighting Foam Research Detailed Summaries." A summary of key findings follows.

Key findings

1. **A number of fluorine-free surfactants have been developed**. These include patents issued for foams consisting of water and a high-molecular-weight acidic polymer (HMWAP), a siloxane-containing foam, and over 250 foams synthesized (these include carbohydrate siloxane surfactants, siloxane and carbosiloxane surfactants, silica-based foam, and a foam concentrate consisting of an acid group and/or a deprotonated acid group and an oliganosilane unit and/or oligosoloxane unit). The Swedish Chemicals Agency survey of foam manufacturers and their products with their ingredients may be helpful to further identify potential alternative surfactants.

2. **The amount of performance testing of fluorine-free foams is limited and the results of available tests show the performance of fluorine-free foams is not consistent across types**. In some cases, fluorine-free foams perform as well as fluorinated foams, and in other cases, fluorine-free foams do not.
    - Some performance tests show that fluorine-free foams perform as well as fluorinated foams.
        - Siloxane-based foam is tested against the German military performance standard and performs as well as fluorinated foams and better than fluorine-free foams on F-34 fuel fires.
        - Performance tests show that siloxane-based foams perform better on F-34 fuel fires than nonaqueous film-forming Class B foam.
        - In fire extinguishment and burnback tests of two fluorinated MIL-SPEC foams and one fluorine-free foam on four low-flash-point fuels, the fluorine-free foams perform more consistently than fluorinated foams and the fluorinated foams did not outperform the fluorine-free foams when film formation was not possible.
    - Some performance tests show that fluorine-free foams do not perform as well as fluorinated foams.
        - In a comparison of a fluorine-free foam (Solberg's RF6) to a fluorinated foam (Buckeye Fire Equipment's 3%), the RF6 forms larger bubbles and has a longer drainage time. This may contribute to fuel flux and ignition. RF6 had higher fuel flux across different fuels, and this may be due to RF6 not containing oleophobic surfactants, which are found in fluorinated foams and reject fuel as it transfers through the barriers.
        - In a different, independent test of Solberg's RF6 fluorine-free foam, it struggled to contain vapors well as it does not form a film. Two additional fluorine-free foams (composition confidential and not reported) had erratic performance and placed last in all tested

performance parameters, compared to a fluorinated foam and RF6. The paper noted that in actual practice, foams are reapplied frequently. Performance of both fluorinated and RF6 increased dramatically when reapplied. Therefore, it is suggested that in a practical scenario, rather than under the current testing parameters, RF6 would perform adequately.

3. **The ecotoxicity and impacts on human health of fluorine-free alternatives have not been well characterized or assessed**. Many fluorine-free firefighting water additives contain generic statements that they are preferable to fluorinated foams because they do not contain fluorine. Some of the fluorine-free firefighting wetting agents identified in Section 6 of this report have aquatic toxicity and human health information on the safety data sheet. Safety data sheets for about a quarter of the fluorine-free firefighting water additives could not be obtained. Furthermore, the safety data sheet contains aquatic toxicity information for the formulation and it is unknown how the surfactant itself contributes to human health and ecotoxicity effects. This is a significant gap and identifies a clear research need.

4. **Comprehensive papers exist that expand on performance needs for suppressing Class B fires beyond those included in the Core Performance Standards in this report.**

   - One paper, "The Future of Aqueous Film Forming Foam: Performance Parameters and Requirements," details the reasoning behind the MIL-SPEC performance requirements. Rich with information, this work is highly recommended reading for anyone seeking a deeper investigation into research in this field.
   - "What Properties Matter in Fire-Fighting Foams?" is a resource that provides a list of various properties, why standards have chosen to address them, the reason behind certain values, and the physical properties of concern with foams.

9. Conclusions, Research Needs, and Actions

From the review of firefighting foam performance standards, current and upcoming regulations, identification of fluorine-free foams, other researchers working in this area, and literature, the following conclusions, research needs, and actions have been identified:

1. **Three main information gaps need to be filled to characterize fluorine-free foams in order to promote them as safer alternatives to fluorinated foams:**
   a. **Performance data is uncertain and/or lacking.**
   Research need: Independent testing of fluorine-free foams to validate existing claims and test against others. The U.S. MIL-SPEC and IMO standards are the only performance specifications that require fluorinated surfactants. Performance testing of fluorine-free foams is needed to understand if the performance specifications can be met without the use of fluorinated surfactants. Some fluorine-free foams identified in this report indicate they meet performance specifications. There is some doubt in the firefighting foam industry that fluorine-free foams do in fact meet the standards. Independent performance testing to validate these claims would be beneficial. If foams cannot meet the specification, the testing process will identify exactly what parameter(s) is not being met. Performance testing fluorine-free foams is critical, as the FAA's Reauthorization Act of 2018 no longer requires major FAA airports to use fluorinated foams.
   b. **The makeup of foams is incomplete as many ingredients are protected as confidential business information. Many researchers and those in the firefighting foam industries have raised a concern about whether foams are truly fluorine-free or not.**
   Research need: Identify all fluorine-free foam ingredients and verify they are truly fluorine-free. Ingredients lists present on the safety data sheets of the fluorine-free foams identified in this study were reviewed. Many foams have incomplete lists, as ingredients are deemed confidential business information and excluded. Listing proprietary ingredients makes it impossible to characterize the fluorine-free alternatives to ensure promoted alternatives do not result in regrettable substitution, where one hazardous or toxic ingredient (in this case, fluorinated surfactants) is replaced with another ingredient possessing different hazard characteristics. There is some doubt within the firefighting foam industry that fluorine-free foams are truly free of fluorine. Analyzing a subset of foams would shed light on this concern and help to understand if the foams are completely free of fluorine or if they contain trace amounts.
   Research need: Achieve transparency of ingredients through credible third-party evaluation. Manufacturers may be amenable to an independent, third party evaluating confidential ingredients and formulations in order to report any hazard information without releasing proprietary ingredients and product formulations. This allows users to make informed decisions without releasing confidential business information.
   c. **The ecotoxicity and impacts on human health of most fluorine-free foams and their ingredients have not been characterized or assessed.**
   Research need: Characterize ecotoxicity and human-health impacts of fluorine-free foams, ingredients, and degradation products through third-party hazard and exposure evaluations. Most fluorine-free foams have generic statements that fluorine-free alternatives are preferable because they do not contain fluorine. Some of the fluorine-free foams identified in this report have aquatic toxicity and human-health information available on their safety data sheet. Safety data sheets could not be obtained for all products. Having complete ingredient lists or

formulations disclosed to a third party for analysis is critical to ensure the whole formulation is assessed. Again, characterizing alternative foams will help to eliminate regrettable substitutions.

2. **The use of performance standards across industries is not well understood and characterized.**
   Research need: Dig deeper into mapping performance specifications to applications. A cursory list of industries and situations to which each performance standard applies is included in this report. Reaching out to industry stakeholders, firefighters, and foam manufacturers to validate and expand this list would help to build an understanding of the performance needs for specific fire situations, which could then be used to determine the appropriate foam type for that need.
3. **It is unclear if gaps or discrepancies exist in the performance needs for extinguishing Class B fires and existing performance specifications.**
   Research need: Compare the performance needs and existing performance specifications. It is unclear if performance standards are too strict, not strict enough, or sufficient in all areas of fire suppression. Comparing the needs to standards, such as MIL-SPEC and UL 162, may identify gaps and discrepancies. Working with users knowledgeable about fire suppression needs, foam manufacturers, performance specification authors, and other stakeholders would ensure specifications are appropriate for all.
4. **Organizations are developing fluorine-free foams, characterizing them, and performing alternatives assessments. Washington is the first U.S. state to ban the sale of fluorinated foams.**
   Action: Monitor work by other organizations. The DoD's research to develop and characterize fluorine-free foams, PERF's alternatives assessment of fluorine-free foams, and CPA's work to develop a list of preferable PFAS-free foams are all notable and currently ongoing. The State of Washington is getting ready to implement their ban on the sale of fluorinated foams in 2020 and is currently working to assess alternatives. Their outcomes may be adopted by others and influence policy and product formulations. The landscape is rapidly changing and there may be other organizations in the near future doing similar work.
5. **There is no regulation preventing the use of fluorine-free foams by non-military users, including firefighting training centers, chemical manufacturers, oil refineries, and others.**
   Action: Assist training centers and other non-military users in switching to fluorine-free alternatives. Firefighting training centers do not have to follow the same performance standards as other users and typically use foams that are not certified to a performance standard. There is no regulatory roadblock for training centers to use fluorine-free foams.

Appendix A: Additional Performance Standards

APSAD R12. France. APSAD R12 is concerned with automatic high-expansion foam extinguishing installations. The rule stipulates the design, construction, commissioning, periodical checking, and maintenance requirements of fixed, automatic, high-expansion foam extinguishing systems installed in buildings in the industrial, commercial, agricultural, or tertiary sectors. English version of the standard is not available. Only one mention of this standard was found during the project, so it has very limited application. Learn more: http://www.cyrus-industrie.com/non-classe-en/apsad-r12-4447

CAN/ULC-S564 Standard for Categories 1 and 2 Foam Liquid Concentrates. Canadian standard: https://www.scc.ca/en/standardsdb/standards/23093

CAP168 Licensing of Aerodromes. UK standard: https://www.folkestone-hythe.gov.uk/webapp/lydd-airport/CORE%20DOCS/CD16/CD16.1.pdf

Class A: Ceren Certificate. Forest fire standard: http://www.valabre-ceren.org/

Draves Test AATCC 17-2005. Efficiency of ordinary commercial wetting agents. Learn more: https://members.aatcc.org/store/tm17/484/

FM 5130 Foam Extinguishing Systems. Complex standard covering foams in their entirety from suppression system to concentrate. Referenced once throughout project duration. Learn more: https://www.fmapprovals.com/approval-standards

GB15308-94: General specification for Foam Extinguishing Agents. Standards Administration of China. Referenced once throughout project duration. See standard: https://standards.globalspec.com/std/143880/sac-gb-15308-94

GESIP. Based in France with a French website, this standard was developed by an oil and chemical industry safety research group that shares feedback, and provides training and information. It has been difficult to glean information; appears they certify companies to standards with respect to the oil industry. It is similar to LASTFIRE. Learn more: http://gesip.com/

IMO MSC.1/Circ 1312. Provides some standard information with respect to foams utilized by boats. It seems that, if this standard is met, then the foam is acceptable for ship use, though it does not include other standards associated with suppression systems. Learn more: http://www.imo.org/blast/blastDataHelper.asp?data_id=25955&filename=1312.pdf.

IMO MSC/Circ.670: Guidelines for the Performance and Testing Criteria and Surveys of High-Expansion Foam Concentrates for Fixed Fire Extinguishing Systems. While it is unclear if this is an outdated version of the IMO MSC.1/Circ 1312 or just very similar to it, it is not necessary to consider it individually. Learn more: http://imo.udhb.gov.tr/dosyam/EKLER/MSC-Circ.670.pdf

LASTFIRE. Standard focused on fires with respect to hydrocarbon fuels. Developed by petrochemical companies and designed with constraints less focused on emergency (life-threatening) situations. Learn more: http://www.lastfire.co.uk/

Lloyd's Register. Independent organization that certifies to ISO standards. Learn more: https://www.lr.org/en/

Marine: Veritas/BV. Independent organization that certifies products/companies to ISO/IMO standards. It appears certification by this company means that the vessel is following all standards necessary for the use of foam on a ship. Learn more: https://www.bureauveritas.com/marine-and-offshore

MED Wheelmark. Independent organization that certifies European Union maritime vessels. Learn more: http://www.ecosafene.com/EN/firetesting/marine/262.html

NFPA 1145 Guide for the Use of Class A Foam in Firefighting. This guide assists fire departments and wildland fire agencies in the safe and effective use of Class A foams for manual structural firefighting and protection. Foam application is outside the scope of this project. Learn more: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=1145

NFPA 1150 Standard on Foam Chemicals for Fires in Class A Fuels. This standard defines the acceptance requirements and test methods for fire-fighting foam chemicals that are used to control, suppress, or prevent fires in Class A fuels. May be a fluorine-free standard. Learn more: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=1150

NFPA 18 Standard on Wetting Agents. Provides requirements for the performance and use of wetting agents as related to fire control and extinguishment. It is intended for the guidance of the fire services, authorities having jurisdiction (AHJs), and others concerned with judging the acceptability and use of any wetting agent offered for such a purpose. It could be applied to film-forming foams, but it may not be ideal since it is very broad in scope. Learn more: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=18

NFPA 298 Standard for Foam Chemicals for Wildland Fire Control. Specifies requirements and test procedures for foam chemicals used in wildland firefighting. The standard is most likely concerned with Class A fires, so fluorosurfactants would not be as vital to its assessment. It may be a fluorine-free standard. Learn more: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=298

UK 42-42. UK Military spec firefighting foam that was replaced by EN 1568.

U.S. Department of Agriculture Forest Service Specification 5100-307a Specification for Fire Suppressant Foam for Wildland Firefighting (Class A Foam). This standard outlines requirements for foams utilized for Class A fires. It contains biodegradability requirements, which means that foams meeting this standard are not likely to contain fluorosurfactants. It may inadvertently be a fluorine-free standard. Learn more: https://www.fs.fed.us/rm/fire/wfcs/documents/307a.pdf

USC/CNC; USL/CNL. Unable to find information on these standards. The foam manufacturer FireAde lists them on their website: http://pro.fireade.com/products/fireade/

Appendix B: Core Performance Standards Details

This section includes a summary of each core performance standards along with key text and table excerpts from the standards.

B.1 Australian Government DEF (AUST) 5706

Guidelines for testing fixed Aqueous Film Forming Foam (AFFF) suppression systems

Australia military standard. Criteria similar to ISO. Updated in 2018. Accessible here: http://www.defence.gov.au/EstateManagement/Governance/Policy/EngineeringMaintenance/FireProtection/Guidelines/GuidelinesForTestingFixedAqueousFilmFormingFoam(AFFF)SuppressionSystems.pdf

These guidelines are for testing fixed Aqueous Film Forming Foam (AFFF) monitor, overhead deluge, and pop-up sprinkler fire suppression systems in Australian Defense hangars. They include general guidance in relation to testing, commissioning tests, and requirements for storage, collection, treatment, and disposal of AFFF and AFFF wastewater.

The National Fire Protection Association (NFPA) 11—Standard for Low-, Medium-, and High-Expansion Foam is the internationally and locally acknowledged relevant standard. These guidelines endorse and supplement the general testing provisions included in NFPA 11. In the event of conflict between the requirements of NFPA 11 and the guidelines set out in DEF (AUST) 5706, the latter prevails.

B.2 European Standard EN 1568, Parts 1–4

A general-use standard developed by the European Union to replace the individual standards that each country had possessed. Updated in 2018. Available for purchase here: https://www.en-standard.eu/

- Not a pass or fail standard: Concentrates are given performance grades (in other words, Grades 1-4 for extinguishing performance and Grades A-D for burnback resistance). **Grade 1A is the highest achievable grade**.
- EN 1568-approved products are not conformance monitored after accreditation.
- **Part 1** applies to medium-expansion foam for use on water-immiscible liquids.
- **Part 2** applies to high-expansion foam for use on water-immiscible liquids.
- **Part 3** applies to low-expansion foam for use on water-immiscible liquids.
- Requires a 4.52 m^2 heptane fire with a pre-burn of 60 s to be extinguished at an application rate of 2.52 $L/min/m^2$ using foam with potable and sea water.
- **Part 4** applies to low-expansion foam for use on water-miscible liquids.
- Requires a 1.72 m^2 acetone fire with a preburn of 120 s to be extinguished at an application rate of 6.6 $L/min/m^2$ using foam with potable and sea water.

EN 1568-1	
Sediment Before/After Ageing	0.25%/1%
Viscosity:	
Newtonian	>200 mm^2/s
Psuedo Plastic	120 mPa*s
pH	6.0-9.5
Extinction Time	>120 s
1% Burnback	<30 s

EN 1568-2	
Sediment Before/After Ageing	0.25%/1%
Viscosity:	
Newtonian	>200 mm^2/s
Psuedo Plastic	120 mPa*s
pH	6.0-9.5
Extinction Time	>150 s

EN 1568-3					
Extinguishing Performance Class	**Burnback Resistance Level**	**Gentle Application Test**		**Forceful Application Test**	
		Extinction Time Not More Than	**25% Burnback Time Not Less Than** (min)	**Extinction Time Not More Than**	**25% Burnback Time Not Less Than** (min)
I+	A	▨	▨	1.5	10
	B	▨	15	1.5	▨
	C	▨	10	1.5	▨
	D	▨	5	1.5	▨
I	A	▨		3	10
	B	▨	15	3	▨
	C	▨	10	3	▨
	D	▨	5	3	▨
II	A	▨	▨	4	10
	B	▨	15	4	▨
	C	▨	10	4	▨
	D	▨	5	4	▨
III	B	5	15	▨	▨
	C	5	10	▨	▨
	D	5	5	▨	▨

EN 1568-4			
Extinguishing Performance Class	**25% Burnback Resistance Level**	**Extinction Time Not More Than** (min)	**25% Burnback Time Not Less Than** (min)
I	A	3	15
	B	3	10
	C	3	5
II	A	5	15
	B	5	10
	C	5	5

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B.3 ICAO: The International Civil Aviation Organization Airport Services Manual

The standard that the aviation industry developed with a focus on rapid extinguishment. It is primarily used in airports and was developed to minimize potential danger to those on flights. It provides recommendations and classifications A-C for firefighting foams as well as other best practices for airports. It is internationally applied, though the Federal Aviation Administration (FAA) is U.S. centric. It was last updated in 2014. Available here: https://www.docdroid.net/13f3i/icao-airport-services-manual-part-1-rescue-and-fire-fighting.pdf.

- International Civil Aviation Organization (ICAO)-approved products are not conformance monitored after accreditation.
- ICAO Level A requires a 2.8 m^2 fire to be extinguished at an application rate of 4.1 L/min/m^2.
- ICAO Level B requires a 4.5 m^2 fire to be extinguished at an application rate of 2.5 L/min/m^2.
- ICAO Level C requires a 7.32 m^2 fire to be extinguished at an application rate of 1.75 L/min/m^2.
- All levels require a heptane fire with a 60 s preburn and use of potable water.
- Chapter 8 (p. 43) of the manual is of the most interest as it discusses firefighting foams, detailing procedures for storage, transport, application, standard testing, testing conditions, etc.
- **It does not explicitly mention the need for foams to be fluorinated.**
- It includes best practices for airports with respect to firefighting and general safety.
- The following quote outlines the manual's specific requirements for foam-concentrate performance:

> For each performance level, a foam concentrate is acceptable
>
> > a) if the time to extinguish the fire from the overall surface of the tray is equal or less than 60 s, and b) the re-ignition of 25% of the tray surface is equal to or longer than five minutes. (Note for testing authorities: At the 60 s time, minute flames (flickers) visible between the foam blanket and the inner edge of the tray are acceptable.)
> >
> > a) if they [flickers] don't spread in a cumulative length exceeding 25% of the circumference of the inner edge of the tray, and b) they [flickers] are totally extinguished during the second minute of foam application.

ICAO Performance Specifications

Fire Tests	Performance Level A	Performance Level B	Performance Level C
Nozzle (Air Aspirated)			
Branch Pipe	"Uni 86" Foam Nozzle	"Uni 86" Foam Nozzle	"Uni 86" Foam Nozzle
Nozzle Pressure	700 kPa	700 kPa	700 kPa
Application Rate	4.1 L/min/m2	2.5 L/min/m2	1.56 L/min/m2
Nozzle Discharge Rate	11.4 L/min	11.4 L/min	11.4 L/min
Fire Size	2.8 m2 circular	4.5 m2 circular	7.32 m2 circular
Fuel (on Water Substrate)	Kerosene	Kerosene	Kerosene
Preburn Time	60 s	60 s	60 s
Fire Performance			
Extinguishing Time	< 60 s	< 60 s	< 60 s
Total Application Time	120 s	120 s	120 s
25% Reignition Time	> 5 min	> 5 min	> 5 min

B.4 IMO: International Maritime Organization

Guidelines for the Performance and Testing Criteria and Surveys of Foam Concentrates for Fixed Fire-Extinguishing Systems

Follows similar criteria to ISO and largely focuses on how to perform the tests. Updated in 2009.

The IMO standards are focused on merchant ships and are required by many maritime administrations and classification bodies for foam concentrates to be used on board ships in international waters. They arose as part of the implementation of the Safety of Life at Sea (SOLAS) Convention.[22] There are 174 member states that follow IMO.

- **Explicitly calls out aqueous film-forming concentrate as having fluorinated surfactants**
- **IMO MSC Circ.670** sets out the testing protocols and acceptance criteria for the testing of high-expansion foam concentrates. Find further information here: http://imo.udhb.gov.tr/dosyam/EKLER/MSC-Circ.670.pdf
- The standards are now required by many maritime administrations and classification bodies for foam concentrates to be used on board ships in international waters and have arisen as part of the implementation of the SOLAS Convention.

IMO Specifications	
Sedimentation	≤ 0.25% by volume
Kinematic Viscosity	Max: 200 mm^2/s
pH	6 < pH < 9.5 at 20 °C
Spreading Coeffcient	> 0 N/m
Expansion Ratio Parameters:	
Flow Rate	11.4 L/in
Nozzle Pressure	6.3 ± 0.3 bar
Extinction Time	≤ 5 min
Burnback Time	> 15 min for 25% of the surface
Mass Density	ASTM D 1298-85 (reference)

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[22] Read the International Convention for the Safety of Life at Sea (SOLAS), 1974 here: http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-(SOLAS),-1974.aspx

B.5 ISO-7203

Fire Extinguishing Media: Foam Concentrates

International focus. Updated in 2011.

The International Standards organization developed a general use standard with respect to foam performance. These were not developed with a singular specific purpose and the multitude of classes provide variety in how well the foam will perform so that buyers will know exactly what they are getting. Below are the ISO's specifications in detail.

ISO 7203-1 Specification for low-expansion foam concentrates for top application to water-immiscible liquids (Full document: http://iso-iran.ir/standards/iso/ISO_7203_1_2011_,_Fire_Extinguishing.pdf)

ISO Max Extinction Times and Min Burnback Times (min)					
Extinguishing Performance Class	Burnback Resistance Level	Gentle Application Test		Forceful Application Test	
		Extinction Time Not More Than	25% Burnback Time Not Less Than (min)	Extinction Time Not More Than	25% Burnback Time Not Less Than (min)
I	A	Not applicable		3	10
	B		15	3	Not applicable
	C		10	3	
	D		5	3	
II	A	Not applicable		4	10
	B		15	4	Not applicable
	C		10	4	
	D		5	4	
III	B		15	Not applicable	
	C		10		
	D		5		

ISO 7203-2 Specification for medium- and high-expansion foam concentrates for top application to water-immiscible liquids (Full document: http://iso-iran.ir/standards/iso/ISO_7203_2_2011_,_Fire_Extinguishing.pdf)

Types of Expansion Foam	Medium Expansion Foam	High Expansion Foam
Extinction Time (s)	Not more than 120	Not more than 150
1% burnback Time (s)	Not less than 30	Not applicable

ISO 7203-3 Specification for low-expansion foam concentrates for top application to water-miscible liquids (Full document: (Full document: http://iso-iran.ir/standards/iso/ISO_7203_3_2011_,_Fire_Extinguishing.pdf)

Extinguishing Performance Class	Burnback Resistance Level	Extinction Time Not More Than (min)	25% Burnback Time Not Less Than (min)
I	A	3	15
	B	3	10
	C	3	5
II	A	5	15
	B	5	10
	C	5	5

B.6 LASTFIRE Hydrocarbon Storage Tanks

Updated in 2015. Accessible here: http://www.lastfire.org.uk/uploads/LFTestSpecRevD-APR2015.pdf

The LASTFIRE standard emerged when a consortium of oil industry leaders came together to provide accurate information on firefighting foams. ("LAST" is an acronym for Large Atmospheric Storage Tank.) More of a "best practices" guide than a set of standards, it ranks foams from 0–100. It is focused on atmospheric tank fires and, as a result, is more concerned with how foams will behave and degrade over a long period of time than with rapid extinguishment.

- The project was initiated due to the oil and petrochemical industries' recognition that the fire hazards associated with large-diameter, open-top, floating-roof tanks were insufficiently understood to be able to develop fully justified site-specific fire-response and risk-reduction policies.
- Part of this project was to develop a foam-testing protocol in order to assess a foam's capability to achieve the special performance characteristics relevant to large storage tank firefighting.
- The LASTFIRE test was rapidly established as a standard for this severe application and has been included as a requirement in foam concentrate procurement specifications by major international oil companies.
- Applications are focused on putting out fires in open-top fuel tanks
- Ratings are based on a scale of 100% effectiveness (p. 13)
  - Fire control: 5%
  - Extinguishment capability: 65%
  - Post-extinguishment vapor suppression: 15% (2 trials of 7.5% each)
  - Burnback resistance: 15%
  - These values were based on polls of experienced operators and what they felt was important in the foams.
- 100–80% is considered "Good Fire Performance."
- 79.5–50% is considered "Acceptable Fire Performance."
- 49.5–25% is considered "Reduced Fire Performance."
- 24.5–0% is considered "Poor Fire Performance" (p. 21).

LASTFIRE Criteria	Minutes from ignition	Score	Remarks
Fire Control	0-5	5	
	>5-8	2	
	8-10	0	
	>10	FAIL	Overall Fail
	Maximum score	***5***	***5% of total***
Extinguishment	0-6	65	
	>6-10	55	
	>10-12	45	
	>12-20	25	
	20-30	15	
	>30	FAIL	Overall Fail
	Maximum score	***65***	***65% of total***
Vapor Suppression	**Test One**		
		7.5	*No reignition*
		5	*Minor edge ignition only*
		2.5	*Full circumference ignition or single ghosting over surface*
		0	*Full flash and prolonged ghosting over surface*

LASTFIRE Criteria	Minutes from ignition	Score	Remarks
	Maximum score	***7.5***	***7.5% of total***
	Test two - scoring as test one		
		7.5	*No reignition*
		5	*Minor edge ignition only*
		2.5	*Full circumference ignition or single ghosting over surface*
		0	*Full flash and prolonged ghosting over surface*
		OVERALL FAIL	*Significant prolonged flaming 25-50%, flames>pan*
	Maximum score	***7.5***	***7.5% of total***
Burnback Resistance		15	*<25%, minor flaming*
		10	*<25% flash/<65% circ.*
		5	*Flash 25-50%/<65% circ.*
		0	*Full flash/continued ghosting 25-50%*
		OVERALL FAIL	*Full flash/sustained flaming or ghosting >50%/exposed fuel >10%, iceberging*
	Maximum score	***15***	***15% of total***
	Total	**100**	

Below are extracts from LASTFIRE regarding specific topics.

Fire control:

> Marks are awarded for the foam's ability to achieve 90% control up to a maximum of eight min from ignition (in other words, 5 min [of] foam application). Foams controlling the fire in 8–10 min (5–7 minutes of foam application) are given no marks in this section. Those foams that fail to control the fire once foam application has ceased even after 30 minutes from ignition are deemed to have "failed" the requirements of the LASTFIRE test and given a resultant zero overall score.

Extinguishment:

> Recognising that extinguishment of the fire is the ultimate aim of foam application and, generally speaking, the sooner it is achieved the better, scoring shall be based on a "sliding scale" with full marks given for extinguishment during the first three minutes of foam application (up to 6 min from ignition). If extinguishment is not achieved within the full 30 min test, then the foam is classified as "FAIL" and given an overall zero score.

Vapor suppression:

> Vapor suppression performance shall be assessed in the LASTFIRE test by passing a lighted torch around the full circumference and centre of the foam blanket. This shall be done twice during the test and each test [will be] given a maximum possible 7.5% of the total test marks. The extent of reignition shall be evaluated and scores given for each "torch test" based on the following observations:
>
> - Seven-and-a-half marks for no reignition
> - Five marks for < 65% of the circumference of the pan reignition which then extinguish and are not taller than the pan height.
> - Two-and-a-half marks for > 65% of the circumference of the pan reignition or minor "ghosting" occurs which is short lived and extinguished rapidly.

- Zero marks for full flashover if flames subside rapidly or > 65% of the circumference ignites with flames greater than the pan height that persist, or ghosting is persistent but not greater than the height of the pan.
- "OVERALL FAIL" shall be deemed if significant, prolonged flaming over a large proportion of the surface (25–50 %) is observed, with flames greater than the test pan height. "OVERALL FAIL" shall be given, even if flaming subsides, and subsequent seal or burn back tests can be conducted.

Burnback resistance:

> Different foams are able to resist "burnback" to varying degrees. Upon removal of the burnback pot (and in some cases before removal) foams can exhibit minor or extended reignition of the foam blanket. In some cases, the fuel surface will be exposed as subsequent foam "layers" are burnt and deteriorate. . . . Marks shall be awarded for burnback resistance as follows:
>
> - Fifteen marks for < 25% of reignition at any point during test, no full surface flash, minor flickers no greater than the height of the pan are allowed, <65% of circumference flash with flames no greater than the height of the pan, and no visible fuel is observed.
> - Ten marks for < 25% of reignition with a full flash permitted if it subsides slowly and <25% continues to burn, < 65% of circumference burns and flames are less than the pan height, and no exposed fuel is observed.
> - Five marks for < 25% of reignition with a full flash permitted if it subsides slowly and <25% continues to burn, < 65% of the circumference burns but the flames are greater than the pan height, and no exposed fuel is observed.
> - Zero marks for 25–50% of the fuel flaming at the end of test, ghosting or flaming is persistent over 25–50% of the test bed, fuel exposure is evident as long as it is < 10% of pan area.
> - OVERALL FAIL shall be deemed if > 50% of the surface area is caught in a full flash or is burning at the end of the test, prolonged surface flames greater than the height of the pan are observed, > 10% fuel exposure is observed, or significant foam deterioration occurs (iceberging).

B.7 NFPA 11 Standard for Low-, Medium-, and High-Expansion Foam

U.S. standard focused on firefighting systems. Updated in 2016. Available for purchase here: https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=11.

This standard was developed with tank fires as the primary concern and is mostly concerned with foam transit time across a hot fuel surface. It covers the design, installation, operation, testing, and maintenance of low-, medium-, and high-expansion foam systems for fire protection. Criteria apply to fixed, semi-fixed, or portable systems for interior and exterior hazards.

B.8 UL 162 Standard for Foam Equipment and Liquid Concentrates

Internationally recognized standard developed and maintained by Underwriters Laboratories Inc. Updated in 2018. Available for purchase here https://standardscatalog.ul.com/standards/en/standard_162.

This is a comprehensive and persistent standard that shows the compatibility of foams and provides firefighting performance specifications. Its requirements cover foam-producing equipment and liquid concentrates employed for the production and discharge of foam that has an expansion ratio of 20:1 or less and is used for fire extinguishment. This standard evaluates specific combinations of foam concentrates and foam equipment together, since performance for a given concentrate may vary depending on equipment-specific factors.

- It is a pass/fail test.
- UL 162 requires a 50 ft^2 heptane fire with a preburn of 60 s to be extinguished at an application rate of 1.63 L/m^2 using a freeze-protected foam with potable and sea water.
- UL-listed products are monitored with samples that are sent to UL every three months for conformance testing. This guarantees the foam being supplied is the same formulation as was originally tested; no other test standard requires this monitoring.

Products that meet the current standard can be found by searching UL category code “GFGV” on the UL Certifications Directory (Access here: http://database.ul.com/cgi-bin/XYV/template/LISEXT/1FRAME/index.html). Each company listing includes the foam products it carries and the equipment that the foams are certified to work with.

B.9 U.S. Federal Aviation Administration (FAA)

The Federal Aviation Administration (FAA) outlines in Title 14, Code of Federal Regulations (CFR) [Part 139] that, in order to issue airport-operating certificates, an airport must

- serve scheduled and unscheduled air-carrier aircraft with more than 30 seats, or
- serve scheduled air-carrier operations in aircraft with more than nine seats but fewer than 31 seats.

Below are resources related to Part 139.

- A list of airports certified under Part 139 can be accessed here: https://www.faa.gov/airports/airport_safety/part139_cert/media/part139-cert-status-table.xls
- Operators of Part 139 airports must provide aircraft rescue and firefighting (ARFF) services during air carrier operations that require a Part 139 certificate. The guidance and resources below address ARFF training, ARFF vehicles, and other aviation fire and rescue requirements.
- General website summarizing ARFF standards: https://www.faa.gov/airports/airport_safety/aircraft_rescue_fire_fighting/
- In Chapter 6 of a 2004 advisory circular outlining performance requirements for Aircraft Fire Extinguishing Agents, the following specifications are outlined:

  > AFFF agents must meet the requirements of Mil-F-24385F. It is important to note that if one vendor’s foam is mixed with another vendor’s foam in the reservicing process, there must be compatibility between foams to prevent gelling of the concentrate.[23]

- The statement below is from a National Part 139 CertAlert [No. 16-05] issued by the FAA in 2016, titled “Update on Mil-Spec Aqueous Film Forming Foam (AFFF).”[24]

  > 3. Actions.
  >
  > a. Airport operators must ensure any AFFF purchased after July 1, 2006, meets MilSpec standards.
  >
  > i. AFFF meets Mil-Spec standards if the AFFF appears on the DoD QPD web site.
  >
  > ii. If the AFFF is NOT on the QPD, the AFFF is NOT authorized for use at Part139 airports.
  >
  > b. However, if a Part 139 airport operator:
  >
  > i. Purchased the previous AFFF standard of UL 162 prior to July 1, 2006, the airport operator can continue to use the current inventory until depleted or the AFFF reaches the manufacturers’ expiration date; or
  >
  > ii. Purchased AFFF listed on the QPD after July 1, 2006, but that AFFF is no longer listed on the current QPD, the airport operator can continue to use the current inventory until depleted or the AFFF reaches the manufacturers’ expiration date.

- Further regulatory information can be found in Title 14, CFR [Part 139.137], titled “Aircraft Rescue and Firefighting: Equipment and Agents.” It contains specifications for vehicles and extinguishing agents and can be found here: https://www.faa.gov/airports/airport_safety/part139_cert/

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[23] Access the advisory circular here: https://www.faa.gov/documentLibrary/media/Advisory_Circular/AC_150_5210-6D.pdf

[24] See the advisory alert here: https://www.faa.gov/airports/airport_safety/certalerts/media/part-139-cert-alert-16-05-Mil-Spec-AFFF-website-update.pdf

B.10 US Military Specification (MIL-SPEC)

MIL-PRF-23485F(SH) w/Amendment 2, 7 Sept 2017

Focused on rapid extinguishment. Developed with the prevention of weapons discharge aboard Navy ships as the primary focus. Approved for use by all departments and agencies of the U.S. Department of Defense (DoD). Only standard that includes maximum PFOA and PFOS content. Available here *http://quicksearch.dla.mil/qsDocDetails.aspx?ident_number=17270*

The following segments from the standard outlines the requirements it specifies:

> 3. REQUIREMENTS 3.2 Materials. Concentrates shall consist of fluorocarbon surfactants plus other compounds as required to conform to the requirements specified hereinafter. The material shall have no adverse effect on the health of personnel when used for its intended purpose.
>
> Total fluorine content of the AFFF shall be determined and shall not deviate more than 15 % of the value determined and reported at time of qualification report.
>
> 4.7.8 PFOA and PFOS content. The tests for PFOA and PFOS content shall be conducted by a laboratory that is accredited by the DoD Environmental Laboratory Accreditation Program (ELAP) and tests in compliance with the "Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water" table of DoD QSM Version 5.1. (A list of ELAP accredited laboratories can be found online at http://www.denix.osd.mil/edqw/accreditation/accreditedlabs. Under the "Method" drop-down list, select "PFAS by LCMSMS Compliant with QSM 5.1 Table B-15.") Test results shall be recorded from the lowest dilution possible while still meeting all of the requirements in the DoD QSM table. This may require results to be recorded from two different dilutions; one for PFOA and one for PFOS.
>
> 6.6 PFOA and PFOS content. The DoD's goal is to acquire and use a non-fluorinated AFFF formulation or equivalent firefighting agent to meet the performance requirements for DoD critical firefighting needs. The DoD is funding research to this end, but a viable solution may not be found for several years. In the short term, the DoD intends to acquire and use AFFF with the lowest demonstrable concentrations of two particular PFAS; specifically PFOS and PFOA. The DoD intends to be open and transparent with Congress, the Environmental Protection Agency (EPA), state regulators, and the public at large regarding DoD efforts to address these matters. AFFF manufacturers and vendors are encouraged to determine the levels of PFOS, PFOA, and other PFAS in their products and work to drive these levels toward zero while still meeting all other military specification requirements.

MIL-SPEC Table 1: Chemical and Physical Requirements for Concentrates or Solutions

Requirement	Values	
	Type 3	Type 6
Minimum Refractive Index	1.3630	1.3580
Viscosity (Centistokes)		
Maximum at 5 °C	20	10
Minimum at °C	2	2
pH	7.0-8.5	7.0-8.5
Minimum Spreading Coefficient	3	3
Foamability:		
Minimum Foam Expansion	5.0	5.0
Minimum Drainage Time, 25 %	2.5	2.5
Corrosion Rate:		

General		
Cold-Rolled Steel, Maximum milli in/yr	1.5	1.5
Copper-Nickel, Maximum milli in/yr	1.0	1.0
Nickel-Copper, Maximum milli in/yr	1.0	1.0
Bronze, Maximum mg	100	100
Localized, Corrosion Resistant Steel	No Pits	No Pits
Perfluorooctanoic Acid (PFOA) Content, Maximum ppb	800	800
Perfluorooctane Sulfonate (PFOS) Content, Maximum ppb	800	800

MIL-SPEC Table 2: Fire Performance			
	AFFF Solutions, percent		
	1.5% of Type 3 3% of Type 6	3% of Type 3 6% of Type 6	15% of Type 3 30% of Type 6
	(Fresh and Sea)	(Fresh and Sea)	(Sea)
28 ft^2 fire:			
Maximum Foam Time to Extinguish	45	30	55
Minimum Burnback Time	300	360	200
50 ft^2 fire:			
Maximum Foam Time to Extinguish		50 (sea only)	
Minimum Burnback Time		360	
Minimum 40 s Summation		320	

MIL-SPEC Qualified Products

There are currently eight MIL-SPEC-qualified products, each available at 3% and 6% concentration. All qualified products contain short-chain (C6) fluorosurfactants. The list of qualified products is available online at http://qpldocs.dla.mil/. Related information is summarized below.

MIL-SPEC Qualified Products	Environmental info, per the manufacturer	Manufacturer
AER-O-WATER 3EM-C6 AFFF AER-O-WATER 6EM-C6 AFFF	C6 Fluorosurfactants National Foam Concentrates do not contain PFOS.	NATIONAL FOAM, INC. 350 E UNION ST WEST CHESTER, PA 193823450 www.NationalFoam.com
TRIDOL-C6 M3 AFFF TRIDOL-C6 M6 AFFF	Angus Fire foam concentrates do not contain PFOS. The C6 surfactants balance high performance and low environmental impact, and are biodegradable.	
ANSULITE AFC-3MS 3% AFFF ANSULITE AFC-6MS 6% AFFF	C6 fluorochemicals manufactured using a telomer-based process that does not produce PFOS. These C-6 materials do not breakdown to yield PFOA compounds.	TYCO FIRE PRODUCTS LP TYCO FIRE PROTECTION PRODUCTS 1 STANTON ST MARINETTE, WI 541432542

MIL-SPEC Qualified Products	Environmental info, per the manufacturer	Manufacturer
CHEMGUARD C306-MS 3% AFFF CHEMGUARD C606-MS 6% AFFF	C6 fluorochemicals are manufactured using a telomer-based process that does not produce PFOS. These C6 materials do not breakdown to yield PFOA compounds. Meets the goals of the UPEPA 2010/15 PFOA Stewardship Program.	
ARCTIC 3% MIL-SPEC AFFF ARCTIC 6% MIL-SPEC AFFF	C6 fluorosurfactants comply with the U.S. EPA 2010/2015 PFOA Product Stewardship Program. Arctic Foam concentrates do not contain PFOS.	AMEREX CORPORATION SOLBERG COMPANY, THE 1520 BROOKFIELD AVE GREEN BAY, WI 543138808 http://www.solbergfoam.com
FIREADE MILSPEC 3 FIREADE MILSPEC 6	Made from 98% organic compounds and zero hazardous chemicals. Encompasses water-based and food-grade ingredients. They are biodegradable and contain no ingredients reportable under the Superfund Amendments and Reauthorization Act (SARA) Title III, Section 313 of 40 CFR-372 or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).	FIRE SERVICE PLUS, INC 180 ETOWAH TRACE FAYETTEVILLE, GA 302145902 http://www.fireade.com
FOMTEC AFFF 3%M "SWE" FOMTEC AFFF 3%M "USA"	Products are biodegradable, formulated with the latest fluorine technology and uses only “All-C6 fluorinated” compounds.	DAFO FOMTEC AB VINDKRAFTSVAGEN 8 STOCKHOLM, 13570 http://www.fomtec.com
PHOS-CHEK 3% AFFF MS PHOS-CHEK 6% MILSPEC AFFF	Made with a mixture of water, hydrocarbon surfactants, solvents, and C6 fluorosurfactants.	ICL PERFORMANCE PRODUCTS LP WILDFIRE CONTROL DIVISION 10667 JERSEY BLVD RANCHO CUCAMONGA, CA 917305110 www.phoschek.com

Appendix C: Core Performance Standards Requirements Comparison

This section contains summary tables of the core requirements of performance standards in order to facilitate easy comparison.

Table C1 contains performance parameters defined in a majority of the standards.

Table C2 contains additional performance parameters that are covered in some, but not all, of the standards.

Table C1. Summary of core performance standards requirements

Standard	Fire Size	Preburn Time	Application Time	Time to Extinguish(s)	25% Reignition Time(s)[a]
DEF (AUST) 5706	4.5 m^2	60	120	50	300
EN 1568-1	1.73 m^2	60	120	120	30 (1% burnback)
EN 1568-2	1.73 m^2	60	120	150	
EN 1568-3 I A	4.52 m^2	60	180	180 (F)	600 (F)
EN 1568-3 I B	4.52 m^2	60	180(F)/300(G)	180 (F)	900 (G)
EN 1568-3 I C	4.52 m^2	60	180(F)/300(G)	180 (F)	600 (G)
EN 1568-3 I D	4.52 m^2	60	180(F)/300(G)	180 (F)	300 (G)
EN 1568-3 I+A	4.52 m^2	60	180	90 (F)	600 (F)
EN 1568-3 I+B	4.52 m^2	60	180(F)/300(G)	90 (F)	900 (G)
EN 1568-3 I+C	4.52 m^2	60	180(F)/300(G)	90 (F)	600 (G)
EN 1568-3 I+D	4.52 m^2	60	180(F)/300(G)	90 (F)	300 (G)
EN 1568-3 II A	4.52 m^2	60	180	240 (F)	600 (F)
EN 1568-3 II B	4.52 m^2	60	180(F)/300(G)	240 (F)	900 (G)
EN 1568-3 II C	4.52 m^2	60	180(F)/300(G)	240 (F)	600 (G)
EN 1568-3 II D	4.52 m^2	60	180(F)/300(G)	240 (F)	300 (G)
EN 1568-3 III B	4.52 m^2	60	300	300 (G)	900 (G)
EN 1568-3 III C	4.52 m^2	60	300	300 (G)	600 (G)
EN 1568-3 III D	4.52 m^2	60	300	300 (G)	300 (G)
EN 1568-4 I A	1.73 m^2	60	180	180	900
EN 1568-4 I B	1.73 m^2	120	180	180	600
EN 1568-4 I C	1.73 m^2	120	180	180	300
EN 1568-4 II A	1.73 m^2	120	300	300	900
EN 1568-4 II B	1.73 m^2	120	300	300	600
EN 1568-4 II C	1.73 m^2	120	300	300	300
ICAO A	2.82 m^2	60	120	60	300
ICAO B	4.5 m^2	60	120	60	300
ICAO C	7.32 m^2	60	120	60	300
IMO	4.5 m^2	60	300	300	900
ISO High Expansion	1.73 m^2	60	120	150	
ISO I A	4.52 m^2	60	180(F)/300(G)	180 (F)	600 (F)
ISO I B	4.52 m^2	60	180(F)/300(G)	180 (F)	900 (G)

Standard	Fire Size	Preburn Time	Application Time	Time to Extinguish(s)	25% Reignition Time(s)[a]
ISO I C	4.52 m^2	60	180(F)/300(G)	180 (F)	600 (G)
ISO I D	4.52 m^2	60	180(F)/300(G)	180 (F)	300 (G)
ISO II A	4.52 m^2	60	180(F)/300(G)	240 (F)	600 (F)
ISO II B	4.52 m^2	60	180(F)/300(G)	240 (F)	900 (G)
ISO II C	4.52 m^2	60	180(F)/300(G)	240 (F)	600 (G)
ISO II D	4.52 m^2	60	180(F)/300(G)	240 (F)	300 (G)
ISO III B	4.52 m^2	60	180(F)/300(G)	▨	900 (G)
ISO III D	4.52 m^2	60	180(F)/300(G)	▨	300 (G)
ISO IIIC	4.52 m^2	60	180(F)/300(G)	▨	600 (G)
ISO Medium Expansion	1.73 m^2	60	120	120	30 (1% burnback)
MIL-SPEC 1.5% Type 3 MIL-SPEC 3% Type 6[b]	28 ft^2	10	90	45	300
MIL-SPEC 15% Type 3 MIL-SPEC 30% Type 6[b]	28 ft^2	10	90	55	200
MIL-SPEC 3% Type 3 MIL-SPEC 6% Type 6 (SEA)[b]	28 ft^2	10	90	30/50 (SEA)	360/360 (SEA)
NFPA 11	NFPA is a very different style of test. Instead of foam being applied via nozzle, foam is instead applied to the fuel surface and the foam is expected to travel across the fuel. NFPA is focused on transit time of the foam, making it more ideal for tank fires but largely unavailable for reporting here.				

*Notes:

[a] (F) is the forceful application of foam, or direct application to liquid fuel and (G) is the gentle application of foam, or application via backboard or other surface.

[b] MIL-SPEC foams must pass all three iterations. To clarify, Type 3 foams must pass tests at 1.5%, 3%, and 15% concentrations and Type 6 foams must pass tests at 3%, 6%, and 30%.

Table C2. Additional core performance standards requirements

	Minimum Refractive Index	Surface Tension, mN/m	Viscosity, Centistokes (maximum/ minimum)	pH	Sedimentation Potential (maximum)	Minimum Spreading Coefficient	Minimum Foam Expansion Ratio	Minimum Drainage Time, 25%, min	Maximum PFOA Content,	Maximum PFOS Content, ppb	LC_{50} Toxicity mg/L (minimum)	COD, mg/L	BOD/COD
DEF (AUST) 5706[a]		0.5 of acceptance testing value	10% of approved manufacturer value	6.5-9									
EN 1568		Within .95x and 1.05x of sampled foam concentrate	200/120 mPa*s (Pseudo Plastic)	6-9.5	0.25% before aging 1% aged			20% of fresh water value					
ICAO			200	6-8.5	0.50%		6-10 film-forming & fluorine-free 8-12 protein based foam	>3 film forming >5 protein based foam					
IMO			200	6-9.5	0.25%	Must be Positive							
ISO		70	200/120 mPa*s (Pseudo Plastic)	6-8.5	0.25% before aging 1% aged	Must be Positive	+ - 20% or + - 1 of manufacturer stated value	+ - 20% of the manufacturer stated time					
MIL-SPEC Type 3[b]	1.363		20/2	7-8.5		3	5	2.5	800	800	500	1000K	0.65
MIL-SPEC Type 6[b]	1.358		2-Oct	7-8.5		3	5	2.5	800	800	1000	500K	0.65

[a] DEF (AUST) 5706 requires corrosion information in the form of mass change. [b] MilSpec also requires corrosion information.

Appendix D: Research Groups & Agencies involved in AFFF Work

This section summarizes the activities from the many organizations in the United States and abroad that are actively engaged in fluorine-free AFFF work. It is recommended that readers follow up directly with the organizations listed as their work progresses and new information emerges.

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D.1 Intergovernmental Organizations

OECD/UNEP Global PFC Group

URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

The OECD/UNEP Global PFC Group was established in 2012 and brings together experts from OECD-member and non-member countries in academia, governments, industry, and within the NGO sectir, as well as representatives from other international organizations.

It was created in response to the International Conference on Chemicals Management (Resolution II/5) (See details of conferences here: https://old.saicm.org/index.php?option=com_content&view=article&id=218:iccm2-outcomes-and-follow-up&catid=89:iccm-2), calling upon intergovernmental organizations, governments and other stakeholders to:

> …consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible.

The Group's online portal serves to facilitate the exchange of information on per- and polyfluorinated chemicals, focusing specifically on PFAS. It provides information on the following areas:

1. What are PFAS? (URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/)
2. Risk reduction approaches (URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/riskreduction/)
3. Alternatives (URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/alternatives/)
4. Production and emissions (URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/countryinformation/)
5. Information from countries (URL: http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/countryinformation/)

Information provided in the portal comes principally from the work done within the context of the Group.

The OECD released their updated New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances (PFAS) and accompanying methodology report in May 2018. http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/

Interstate Technology Regulatory Council (ITRC)

PFAS Fact Sheets

URL: https://pfas-1.itrcweb.org/fact-sheets/

Fact sheets summarize the latest science and emerging technologies for PFAS and are tailored to the needs of state regulatory program personnel who are tasked with making informed and timely decisions regarding PFAS-impacted sites. Content is also useful to consultants and parties responsible for the release of these contaminants, as well as community stakeholders.

An Introductory document (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_introductory__11_13_17.pdf) has been prepared that briefly describes the contents of each of the fact sheets.

- Naming Conventions and Physical and Chemical Properties (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_naming_conventions__3_16_18.pdf) (updated Mar. 16, 2018)
- Regulations, Guidance, and Advisories (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2018/01/pfas_fact_sheet_regulations__1_4_18.pdf) (updated Jan. 4, 2018)
    - Section 4 Tables Excel file (URL: https://pfas-1.itrcweb.org/tables/ITRCPFASFactSheetSect4TablesNovember17.xlsx) (published Nov. 2017)

    - Table 4-1 presents the available PFAS water values established by the U.S. EPA, each pertinent state, or country (Australia, Canada, and Western European countries)
    - Table 4-2 presents the available PFAS soil values established by the U.S. EPA, each pertinent state, or country (Australia, Canada, and Western European countries)
    - Section 5 Tables Excel file (URL: https://pfas-1.itrcweb.org/tables/ITRCPFASFactSheetSect5TablesNovember17.xlsx) (published Nov. 2017)
    - Table 5-1 summarizes the differences in the PFOA values for drinking water in the United States.
    - Table 5-2 summarizes the differences in the PFOS values for drinking water in the United States.
- History and Use (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf) (published Nov. 13, 2017)
- Environmental Fate and Transport (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_fate_and_transport__3_16_18.pdf) (published Mar. 16, 2018)
    - Table 3-1 Log Koc values for select PFAS Excel file (published Apr. 2018)
- Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf) (published Mar. 15, 2018)
- Remediation Technologies and Methods (URL: https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_remediation_3_15_18.pdf) (published Mar. 15, 2018)
    - Remediation Comparison Tables (published Apr. 2018), Table 1 – Solids Comparison & Table 2 – Liquids Comparison
- Aqueous Film-Forming Foam (expected soon)

D.2 Government

US Department of Defense

Environmental Research Programs on PFAS by the Strategic Environmental Research and Development Program (SERDP)

URL: https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs

Project objectives are identified in annual statements of need. The AFFF formulation projects are in the "Weapons Systems and Platforms" program area (See: https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/(list)/1/). Some projects contain additional information and are organized by "Active Projects" and "Completed Projects" on the program-area web page. No recent AFFF projects were identified among the "Completed Projects" group (accessed May 2018). Projects related to AFFF under the "Active Projects" group are detailed below by start year.

Contact:
Robin A. Nissan, Ph.D.
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Alexandria, VA 22350-3605
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"Fluorine-Free Aqueous Film-Forming Foam"
FY 2017 Statement of Need Projects

URL: https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Contaminated-Groundwater-SONs/Film-Forming-Foam-PFAS-WP

The projects listed below were selected to address the objectives of this Statement of Need.

“WP-2737 Novel Fluorine-Free Replacement for Aqueous Film Forming Foam”
The objective of this project is to demonstrate proof-of-concept for the development of the next generation of fluorine-free firefighting foam formulations as a replacement for existing AFFF. The novel foam systems produced in this research are derived from polysaccharide copolymers and nanoparticles (based on chitosan) that are sustainable, non-toxic, water-soluble (or water-dispersible) and will be applied using existing military firefighting equipment. These foam systems will meet or exceed both environmental regulations and firefighting performance defined in military specification (MIL-SPEC) MIL-F-24385F “Military Specification: Fire Extinguishing Agent, Aqueous Film Forming Foam (AFFF) Liquid Concentrate, For Fresh and Seawater” (1994).

Principal Investigator: Dr. Joseph Tsang, NAVAIR, Phone: 760-939-0256, joseph.tsang@navy.mil

Status (April 2018): This project started in January 2017 and reportedly is complete. No report is available at this time (personal communication, Robin Nissan, SERDP). Additional project description is available here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2737

“WP-2738 Fluorine-Free Aqueous Film Forming Foam”
The environmental issue to be addressed in this project is the use of fluorosurfactants and fluoropolymers in AFFF for fire suppression. All foams that meet the requirements of MIL-F 24385 must contain fluorocarbons. Older formulations contain C8; newer products have shorter C6 fluorocarbon chains. C6 fluorocarbons are persistent in the environment, but their toxicology to humans and aquatic species is considered more benign than C8. A fire-fighting foam that genuinely biodegrades in the natural environment would eliminate any future concerns.

The objective of this project is to use scientific methods to increase understanding of the physical and chemical processes that underlie fire-fighting foams and how the components of a foam formulation can deliver the properties required for good fire performance while minimizing environmental burdens. Statistical methods will be employed to develop a fluorine-free surfactant formulation that meets the performance requirements defined in MIL-F 24385.

A life-cycle assessment (LCA) will compare the environmental impact of each foam type and identify routes to improving environmental performance.

Principal Investigator: John Payne, National Foam, john.payne@aisafetygroup.com

Status (April 2018): This project began January 2017 and is expected to continue through 2019. A detailed project plan was provided by the principal investigator (PI) and is available among the IC2 project documents. The project LCA is nearly complete, and the PI provided a poster summary. Formulation work should be complete in mid-to-late 2019. Quick results are expected through the use of existing commercial surfactants rather than new, synthesized formulations. A project summary can be found here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2738

“WP-2739 Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression”
The objective of this project is to develop a fluorine-free, firefighting surfactant formulation that meets the performance requirements of MIL-F-24385F and is an environmentally friendly, drop-in replacement for the current environmentally hazardous AFFF.

This project will build on U.S. Naval Research Laboratory (NRL) experience and on the toxicology and analytical capabilities of Oregon State University in a dual-track approach to identify and develop fluorine-free surfactants with both fire suppression effectiveness and low environmental impact. The investigators will choose oxyhydrocarbon and siloxane surfactants from commercial sources where available or synthesize at laboratory scale. Investigators employ a tiered-approach, wherein the number of candidate surfactants taken forward will be reduced at each tier based on the results from modeling, measurements of fire suppression efficiency, and environmental acceptability. They will choose and modify surfactant structures to balance oleophobicity and amphiphilicity to improve suppression of fuel transport through foam and foam stability. They will use QSAR, molecular and continuum dynamics models to select, eliminate, and modify surfactant structures based on acute toxicity and fuel transport through a single lamella (bubble's liquid wall). They will perform prescreening measurements of surfactant solution properties and lamella dynamics to down-select promising surfactants. They will evaluate surfactants by quantifying long-term toxicity, biodegradability, and the fire-suppression effectiveness of the foams at laboratory scale. Finally, investigators will perform the 28-ft^2-pool-fire-suppression test and the aquatic toxicity test according to MIL-F- 24385F and the appropriate ASTM, EPA, OECD methods on the down-selected foam formulations.

Principal Investigator: Ramagopal Ananth, U.S. Naval Research Lab, Phone: 202-767-3197, ramagopal.ananth@nrl.navy.mil

Status (April 2018): The project started in January 2017 and is expected to continue through 2019. The PI provided a number of presentations and documents related to NRL work in the AFFF area (available in the IC2 project files). A project summary can be found here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2739

"Innovative Approaches to Fluorine-Free Aqueous Film Forming Foam"
FY 2018 Statement of Need Projects

The objective of this limited-scope Statement of Need is to develop a fluorine-free surfactant formulation for use in AFFF fire-suppression operations.

URL: https://serdp-estcp.org/content/download/45625/425507/file/WPSON-18-L1%20Fluorine-Free%20AFFF.pdf

Several AFFF projects were identified from the SERDP website with start dates in 2018:

"WP18-1638 Fluorine-free Aqueous Film Forming Foams Based on Functional Siloxanes"
AFFF containing PFOA and PFOS have been traditionally used by the DoD in fuel-fire suppression operations. These chemicals have strong chemical bonds and are considered as persistent, bio-accumulative and toxic (PBT) substances. PFOS/PFOS chemicals have been detected around the world in the food chain, drinking water, animals, and human blood. Therefore, EPA is regulating the chemical industry for the complete elimination of PFOA and PFOS chemicals along with certain C6 substances (containing six fluorinated carbons) by 2015. Therefore, the DoD is seeking non-toxic alternatives—preferably fluorine-free compounds—to replace PFOA/PFOS in firefighting foam formulations. In this project, specifically functionalized siloxane-based surfactants will be synthesized, and their physical and fire suppression abilities will be evaluated. The tests will include the evaluation of 28-ft^2-fire performance, spreading coefficient, aquatic toxicity, chemical oxygen demand (COD), and bio-persistency.

Principal Investigator: Kris Rangan, Materials Modification, Inc., Phone: 703-560-1371

Status (May 2018): The project started in March 2018. No attempt was made to contact the PI.
A project summary can be found here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1638

"WP18-1519 Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foams (F3)"
The objective of this research project is to explore an innovative approach in using polyhedral oligomeric silsesquioxanes (POSS) as drop-in replacements of perfluoroalkyl surfactants found in current AFFF concentrates used in fire-fighting by the DoD. The new POSS surfactants produced in this research will contain only the elements carbon, silicon, hydrogen, and oxygen. Foams containing the new surfactants will extinguish small-scale, unleaded-gasoline pool fires in 45 seconds or less, as dictated by MIL-F-24385F. In addition, the POSS surfactants will have low, acute toxicity to fish and be biodegradable according to measurements of chemical oxygen demand and biological oxygen demand of microorganisms. Commercially available alkylated POSS compounds will be chemically modified with hydrophilic polyethylene glycol (PEG) units. A range of PEG lengths will be used in the selective modification to

determine the proper size range imparting surfactant properties to the PEGylated POSS. By this approach, the organosilicate cage of the POSS surfactants will be targeted to reside at the air-water boundary layer of the bubble lamella in foams. The new POSS surfactants will be characterized by standard analytical techniques (nuclear magnetic resonance [NMR], gas chromatography mass spectrometry [GCMS]). Key physical properties of the POSS surfactants will be measured such as density, surface and interfacial tensions, foam expansion rate, and spreadability. The POSS surfactants will be formulated into AFFF concentrates similar to commercial varieties used by the DoD. The thickness of POSS surfactant film, alone or in concentrate form, supported by hydrocarbon solvent will be measured. Small-fire extinguishing experiments will be conducted to compare the differences (time to extinguish and burnback) between the POSS-based AFFF and the current technology. The small-scale experiments will be a stepping stone to the large MIL-SPEC test (MIL-F-24385F). A preliminary toxicity screening of the POSS surfactants by the Microtox assay and acute toxicity to fish will be made by fee-for-service laboratories.

Principal Investigator: Dr. Matthew Davis, NAWCWD China Lake, Phone: 760-939-0196, matthew.davis@navy.mil

Status (May 2018): The project started in March 2018. No attempt was made to contact the PI.
A project summary can be found here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1519

"WP18-1592 Stability of Fluorine-Free Foams with Siloxane Surfactants for Improved Pool Fire Suppression"
The research team plans to synthesize siloxane surfactants with a systematic structural variation of the head group and quantify the effects on foam degradation, fire extinction, and environmental impact by quantitative structure-property relationships. This knowledge will be used to achieve full coverage of burning pool surface with a siloxane foam. The researchers have been conducting research to identify and develop fluorine-free surfactants having both high fire-suppression effectiveness and low environmental impact. The evaluation of several commercial fluorine-free siloxane surfactants in the last several months has shown that foams made from several of these surfactants exhibit more rapid degradation relative to AFFF containing fluorocarbon surfactants. The rapid degradation prevents these siloxane-based fluorine-free foams from completely covering the liquid fuel surface; full coverage is necessary but not sufficient to extinguish the fire because the foam layer must also block the diffusion of fuel vapors through the foam. Quantifying the effects of systematic and fundamental variations in surfactant structure on foam stability is essential to achieve foam's full coverage of the fuel pool's surface.

This research will synthesize fluorine-free, siloxane-based surfactants by attaching different head groups (cationic, anionic, non-ionic, zwitterionic) to a fixed tail group because the solubility of surfactant in fuel (versus water phase) and stability of the lamellae (bubble walls) within the foam are affected by the charge or polarity of the surfactant's head group. Researchers will also attach different tail groups (straight chain siloxane, trisiloxane with methyl pendant groups, and a trisiloxane with phenyl pendant groups) to the most promising head group to vary the packing density and stiffness of the tail at the lamella surface. They will quantify the effect of both head group and tail group substitution on foam stability. They will also synthesize a straight-chain siloxane with a sulfonate head group and compare its performance with a hydrocarbon analogue (e.g., sodium dodecyl sulfonate); they will test the basic hypothesis that siloxane-based surfactant tails are more effective than hydrocarbon tails for suppressing fuel transport and thus more effective at fire suppression. The research team will use Quantitative Structure Activity Relationships (QSAR) and EPA models to assess the environmental impact of the promising siloxane-based, fluorine-free surfactants.

Principal Investigator: Ramagopal Ananth, U.S. Naval Research Lab, Phone: 202-767-3197, ramagopal.ananth@nrl.navy.mil

Status (April 2018): The project started in March 2018. The PI provided a number of presentations and documents related to Naval Research Laboratory work in the AFFF area (available in the IC2 project files). A project summary can be found here: https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/WP18-1592.

US Naval Research Laboratory (NRL)

NRL is the home of work in the Navy on AFFF, but there may be other work at other branches of the military. NRL has ongoing funding to improve/develop AFFF. In addition to a standing budget, they can apply for and win SERDP funding for environmental projects. They have current projects in fluorine-free foam development and in remediation of PFAS-contaminated sites.

The Navy is not willing to sacrifice performance of foams. They feel that many lives were lost before the introduction of PFAS foams that would have otherwise been saved. They are strongly committed to the existing firefighting infrastructure on ships. Huge costs would be involved in changing the equipment to meet a different set of foam properties. NRL is always willing to evaluate and test the performance of alternatives. Any foam can apply to join the Qualified Products List; suppliers need to pay the costs of the testing work at NRL.

The Navy has considered whether there should be a change in specifications. For example, it might make sense to have a different standard for ships from what is used for land-based applications.

Presentations and Papers

"Molecular Dynamics Simulations of the Fluorinated and Fluorine-free Surfactant Monolayers at Air-Water and Heptane-Water Interfaces" [presentation], 255th ACS National Meeting, New Orleans, LA (March 18-22, 2018), Xiaohong Zhuang, ASEE Postdoctoral Associate and Katherine Hinnant and Ramagopal Ananth, Chemistry Division, U.S. NRL

"Evaluating Foam Degradation and Fuel Transport Rates Through Novel Surfactant Firefighting Foams for the Purpose of AFFF Perfluorocarbon Replacement," Spring Technical Meeting, Eastern States Section of the Combustion Institute, State College, PA (March 4-7, 2018), Xiao Zhuang, ASEE Postdoctoral Associate and Katherine Hinnant, Art Snow, Spencer Giles, and Ramagopal Ananth, Chemistry Division, U.S. NRL

URL: https://blogs.gwu.edu/houston/2018/02/12/evaluating-foam-degradation-and-fuel-transport-rates-through-novel-surfactant-firefighting-foams-for-the-purpose-of-afff-perfluorocarbon-replacement/

"Liquid-Pool Fire Extinction Characteristics of Aqueous Foams Generated from Fluorine-free Surfactants" [presentation], Spring Technical Meeting, Eastern States Section of the Combustion Institute, State College, PA (March 4-7, 2018), Dr. R. Ananth, S. Giles, K. Hinnant, X. Zhuang, A. Snow, J. Fleming, J. Farley, Chemistry Division, U.S. NRL

"Comparison of Firefighting Performance Between Commercial AFFF and Analytically Defined Reference AFFF Formulations" [paper], Katherine Hinnant, Art Snow, John Farley, Spencer Giles, Ramagopal Ananth, U.S. NRL, Washington, DC

"Comparing Firefighting Performance Between Commercial and Analytically Defined AFFF" [presentation and paper], SupDet 2017, College Park, MD (September 14, 2017), Katherine Hinnant, Art Snow, John Farley, Spencer Giles, and Ramagopal Ananth, Chemistry Division, U.S. NRL

URL: https://www.nfpa.org/-/media/Files/News-and-Research/Resources/Research-Foundation/Symposia/2017-SUPDET/SUPDET17-Hinnant-et-al.ashx?la=en&hash=DDE76AC1EC354C8107497344F7DB5309837B5D18

"Development of an Analytical AFFF Formulation" [presentation], 10th US National Combustion Meeting, College Park, MD, April 24, 2017; Katherine Hinnant, Art Snow, John Farley, Spencer Giles and Ramagopal Ananth, Chemistry Division, US Naval Research Laboratory

URL: https://blogs.gwu.edu/houston/2017/04/24/development-of-an-analytical-afff-formulation-for-the-evaluation-of-alternative-surfactants/

“Mechanisms of Fire Suppression with Aqueous Foams and the Role of Surfactants” [presentation], 10th US National Combustion Meeting, College Park, MD, April 24, 2017; Ramagopal Ananth and Katherine Hinnant, Chemistry Division, US Naval Research Laboratory

U.S. Environmental Protection Agency (EPA)

“National Priorities: Per- and Polyfluoroalkyl Substances (PFAS)” Request for Application (RFA)

URL: https://www.epa.gov/research-grants/national-priorities-and-polyfluoroalkyl-substances

Open Date: May 4–June 18, 2018

National Priorities: Per-and polyfluoroalkyl substances

Background: The U.S. EPA released an RFA, “National Priorities: Per- and Polyfluoroalkyl Substances (PFAS).” EPA sought applications that generate new information for nationally assessing PFAS fate and transport, exposure, and toxicity. Per- and polyfluoroalkyl substances (PFASs) are manmade chemicals designed to resist heat, water, and oil. Used in a variety of consumer products and industrial applications, PFASs are moderately-to-highly water soluble, persistent, bioaccumulative, and toxic.

This RFA will inform new strategies that protect public health and the environment from PFAS exposure and adverse outcomes. The EPA anticipates funding approximately two awards under this RFA for a total of $1,984,400. The total project period requested in an application submitted for this RFA may not exceed three years.

For information on eligibility and project specifications, go to https://www.epa.gov/research-grants/national-priorities-and-polyfluoroalkyl-substances

“National Priorities: Per-and Polyfluoroalkyl Substances” is part of EPA’s Safe and Sustainable Water Resources (SSWR) Research Program.

“Research on Per- and Polyfluoroalkyl Substances (PFAS)”

URL: https://www.epa.gov/chemical-research/research-and-polyfluoroalkyl-substances-pfas

Provides brief insight into the efforts being supported by EPA, as well as indicating some of the findings and what role they might play. A summary is below.

- Characterizing and detecting Per and Polyfluoroalkyl substances:
    - EPA developed a Stewardship Program to voluntarily stop producing commercial products that could lead to the generation of PFOA. This was requested after discovery that PFOA was toxic to the environment and poses health risks to both aquatic life and humans.
- Characterizing fate and transport of Per and Polyfluoroalkyl substances:
    - EPA has supported research focused on the degradation of fluorotelomer-based polymers (FTP) into PFOA and PFAS. This research suggests that FTP do break down over time, which was not widely known or supported before the publication. This was largely done through mass spectroscopy method development. The analysis methods can then also be applied so that soil, sludge, plants, animal tissue, and water can be tested for contamination. Initial analysis suggests that using sewage sludge and applying it to agricultural land may be a large contributor to human contamination with PFAS.
- Research on ecological risk from Per and Polyfluoroalkyl substances:
    - The link between PFAS and fish health is largely unclear due to the varied nature of the substances. EPA continues to support research into PFAS impact on fish populations so that policies relating to fish consumption might be developed.
- Exposure from Per and Polyfluoroalkyl substances:
    - EPA works to develop methods to detect PFAS, determine breakdown of PFAS, determine levels of PFAS in a product, and evaluate impact of PFAS on fish populations. Methods already exist to minimize PFAS discharge via wastewater treatment, so the current focus of research is to determine whether biosolids with PFAS can be spread on fields.
- Per- and Polyfluoroalkyl toxicity research with animal models:

    - In the 1980s and 1990s, liver toxicity and tumor development were seen in animals exposed to PFAS as well as stillbirth in pregnant rodents that had been exposed. Biomonitoring also reported elevated levels of PFAS in the general population and in waterways, including those in the Arctic. After additional research, EPA determined that a high level of PFOS exposure would likely cause pulmonary failure in rats/mice while moderate levels would cause retardation in growth and development. PFOA did not produce similar results, but the data was difficult to interpret due to differences between male and female rats and humans. These findings will be used by EPA to generate guidelines, support policies, and support rule-making decisions.
- Using computational modeling for Per- and Polyfluoroalkyl substances research:
    - Computational models are used by EPA to predict what biological effects commonly detected compounds might have to attempt to characterize them. Pharmacokinetic studies are focused on chemical fate within a body. These studies help to show how a chemical will travel, be modified by, and be removed by the body. Comparisons between species can be drawn and overall effects predicted. Overall, these studies have indicated that persistence in the body is proportional to chain length, meaning shorter chains, like PFBA, may be acceptable replacements.

"Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) Under TSCA"

URL: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass

EPA has taken a range of regulatory actions to address PFAS substances in manufacturing and consumer products, as noted below. In addition, EPA worked with eight major leading companies in the PFAS industry to develop and implement a global stewardship program with the goal of eliminating these chemicals from emissions and products by 2015.

- Learn more about EPA's 2010/2015 PFOA Stewardship Program: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass#tab-3
- Read background information on PFAS: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass#tab-2
- Current actions
    - On January 21, 2015, EPA proposed a significant new use rule (SNUR) under the Toxic Substances Control Act to require manufacturers, importers, and processors of PFOA and PFOA-related chemicals (including as part of articles) to notify EPA at least 90 days before starting or resuming new uses of these chemicals in any products. This notification would allow EPA the opportunity to evaluate the new use and, if necessary, take action to prohibit or limit the activity. (See SNUR here: https://www.regulations.gov/document?D=EPA-HQ-OPPT-2013-0225-0001)
    - EPA's New Chemicals Program reviews alternatives for PFOA and related chemicals before they enter the marketplace. Its purpose is to identify whether any new chemicals contain the range of toxicity, fate, and bioaccumulation issues that have been associated with perfluorinated substances in order to avoid any unreasonable risk to health or the environment. (See program documentation here: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/new-chemicals-program-review-alternatives-pfoa-and)
- Previous actions
    - On September 30, 2013, EPA issued a rule requiring companies to report all new uses of certain PFOA-related chemicals as part of carpets, a category of potentially harmful chemicals once used on carpets to impart soil, water, and stain resistance. Companies must now report to EPA their intent to manufacture or import these chemical substances use as part of carpets or to treat carpets. This also includes any importation of carpets already containing these chemical substances. (See SNUR: https://www.regulations.gov/#%21documentDetail;D=EPA-HQ-OPPT-2012-0268-0034)
    - On October 9, 2007, EPA finalized a SNUR on 183 PFAS chemicals believed to no longer be manufactured, imported, or used in the United States. Read more information on the 2007 SNUR for 183 chemicals here: https://www.gpo.gov/fdsys/pkg/FR-2007-10-09/pdf/E7-19828.pdf
    - On March 11, 2002, EPA published a SNUR to require notification to EPA before any future manufacture or import of 13 PFAS chemicals specifically included in the voluntary phase-out of

PFOS by 3M that took place between 2000 and 2002. This SNUR allowed the continuation of a few specifically limited, highly technical uses of these chemicals for which no alternatives were available, and which were characterized by very low volume, low exposure, and low releases. Any other uses of these chemicals would require prior notice to and review by EPA. Read more information on the 2002 SNUR for 13 chemicals: https://www.gpo.gov/fdsys/pkg/FR-2002-03-11/pdf/02-5746.pdf

- On December 9, 2002, EPA published a SNUR to require notification to the agency before any future manufacture or import of 75 PFAS chemicals specifically included in the voluntary phase out of PFOS by 3M that took place between 2000 and 2002. This SNUR allowed the continuation of a few specifically limited, highly technical uses of these chemicals for which no alternatives were available, and which were characterized by very low volume, low exposure, and low releases. Any other uses of these chemicals would require prior notice to and review by EPA. Read more information on the 2002 SNUR for 75 chemicals: https://www.gpo.gov/fdsys/pkg/FR-2002-12-09/pdf/02-31011.pdf

"Fact Sheet: 2010/2015 PFOA Stewardship Program"

URL: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program

In 2006, eight companies committed to attempt to achieve 95% reduction in per- and polyfluoroalkyl substance and any precursor substance emissions by 2010. Additionally, they would attempt to eliminate these chemicals from emissions and products entirely by 2015. Participating companies submitted baseline data, reported annual progress, and agreed to work with the EPA cooperatively. All public documents, including final reports, can be found in EPA Docket EPA-HW-OPPT-2006-0621. All participating companies met the goals of the program. This was achieved by most companies stopping the manufacture and importation of long-chain PFAS. The PFOA Stewardship Program was developed because of concerns with the impact of PFOA and long-chain PFAS on human health and the environment. These concerns developed due to the chemical's persistence, presence in the environment, long half-life in people, and developmental effects in lab animals. The participating companies were Arkema, Asahi, BASP Corporation, Clariant, Daikin, 3M/Dyneon, DuPont, and Solvey Solexis. All of them provided commitments on March 1, 2006, and are global companies. The baseline for comparison purposes was emission- and product-content data from the year 2000. Largely, PFOS and PFOA are no longer manufactured in or imported into the United States, though stocks may exist and still be in use.

"Significant New Use Rules: Long-Chain Perfluoroalkyl Carboxylate and Perfluoroalkyl Sulfonate Chemical Substances"

URL: https://www.regulations.gov/document?D=EPA-HQ-OPPT-2013-0225-0001

The following is an extract from the SNUR titled "Long-Chain Perfluoroalkyl Carboxylate and Perfluoroalkyl Sulfonate Chemical Substances."

> Under the Toxic Substances Control Act (TSCA), EPA is proposing to amend a significant new use rule (SNUR) for long-chain perfluoroalkyl carboxylate (LCPFAC) chemical substances by designating as a significant new use manufacturing (including importing) or processing of an identified subset of LCPFAC chemical substances for any use that will not be ongoing after December 31, 2015, and all other LCPFAC chemicals substances for which there are currently no ongoing uses. For this SNUR, EPA is also proposing to make inapplicable the exemption for persons who import LCPFAC chemical substances as part of articles. In addition, EPA is also proposing to amend a SNUR for perfluoroalkyl sulfonate (PFAS) chemical substances that would make inapplicable the exemption for persons who import PFAS chemical substances as part of carpets. Persons subject to these SNURs would be required to notify EPA at least 90 days before commencing such manufacture or processing. The required notifications would provide EPA with the opportunity to evaluate the intended use and, if necessary, an opportunity to protect against potential unreasonable risks from that activity before it occurs….

> 1. EPA would receive notice of any person's intent to manufacture or process LCPFAC chemical substances, PFOA or its salts, or PFAS chemical substances for the described significant new use before that activity begins.
> 2. EPA would have an opportunity to review and evaluate data submitted in a SNUN before the notice submitter begins manufacturing or processing these chemical substances for the described significant new use.
> 3. EPA would be able to regulate prospective manufacturers or processors of these chemical substances before the described significant new use of the chemical substance occurs, provided that regulation is warranted pursuant to TSCA sections 5(e), 5(f), 6, or 7.

This is the most recent version of the SNUR, but there are older versions that indicate that EPA has been concerned with PFAS use and the resulting chemicals for several years. In brief, notices on imports or business concerning selected compounds must be submitted to EPA so that it can place restrictions on the activity, if necessary. Large business notices are expected to cost no more than $8,589 per notice and, for small businesses, the notices are expected to cost no more than $6,189. EPA developed the SNUR due to concerns with how LCPFAC and PFAS may affect human health and the environment. With the Stewardship Program and the halting of importation via carpets, EPA expects that the presence of PFAS will decline over time. The previous SNURs were implemented in 2007 and 2002, while this latest version is from 2013.

"New Chemicals Program Review of Alternatives for PFOA and Related Chemicals"

URL: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/new-chemicals-program-review-alternatives-pfoa-and

Since 2000, EPA is working to review substitutes to PFOA, PFOS, and long-chain PFAS. The agency focuses on whether the reviewed substances have similar properties to PFOA, PFOS, or long-chain PFAS, and try to determine if the reviewed compound raises any new concerns. These concerns could be related to either health or the environment. Testing of short-chain fluorotelomers includes degradation potential to determine bioaccumulation potential, toxicity, and overall fate compared to PFOA. While previously exempt, polymers containing CF3 or longer chain length fluorinated compounds under the Polymer Exemption Rule can no longer be considered to "not present an unreasonable risk to human health or the environment."

"Final Report: Fluorine-Free Hybrid Surfactants for Fire-Fighting Foams"

URL: https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.highlight/abstract/5089/report/F

The following is an extract from the EPA report titled "Final Report: Flourine-Free Hybrid Surfactacts for Fire-Fighting Foams."

> **Description:** Aqueous film-forming foams (AFFFs) are among the most popular fire-fighting foams used against fuel and oil fires because of their effectiveness and their ease of application. Unfortunately, recent studies have shown that one key ingredient of AFFFs, the fluorosurfactant perfluorooctyl sulfonate (PFOS), is toxic to aquatic life and is a persistent chemical that accumulates in the blood of humans and other animals. Thus, the production of PFOS was stopped in May 2000. Among the phased-out products are 44 fire-fighting foams and foam components. The fire-fighting industry currently is stocked with materials that have been phased out and that, sooner or later, need to be replaced. New fluorosurfactants have been introduced into the market since 2000, and used to formulate aqueous fire-fighting foam concentrates. The toxicity of the new fluorosurfactants and their persistence in the environment are not well established and still are under investigation. Their presence in the future market is unsure. Therefore, the fire-fighting industry has an urgent need for new, environmentally friendly foaming agents and foam stabilizers to replace fluorosurfactants in aqueous fire-fighting foams.

The State of Washington

The State of Washington's Departments of Ecology and Health are working together to develop a chemical action plan that identifies sources and recommends actions to reduce the use, release, and exposure to PFAS in

Washington. The Interim Chemical Action Plan for Per- and Polyfluorinated Alkyl Substances (April 2018) can be found here https://fortress.wa.gov/ecy/publications/summarypages/1804005.html

Washington will be the first U.S. state to ban certain firefighting foams containing perfluorinated compounds beginning in 2018. RCW 70.75A (See here http://app.leg.wa.gov/RCW/default.aspx?cite=70.75A&full=true) was passed in early 2018.

Local Hazardous Waste Management Program in King County, Washington

The Local Hazardous Waste Management Program in King County, Washington, is collaborating closely with Clean Production Action and Toxic-Free Future to reduce exposure to PFAS in firefighting foam by identifying safer alternatives as part of their Safer Alternatives Strategy. King County is also working on reducing exposures to PFAS from food-contact paper and other sources to protect human health and the environment.

New Jersey

"Investigation of Levels of Perfluorinated Compounds in New Jersey Fish, Surface Water, and Sediment"

A report by the New Jersey Department of Environmental Protection, Division of Science, Research, and Environmental Health, SR15-010 (June 18, 2018)

URL:
https://www.nj.gov/dep/dsr/publications/Investigation%20of%20Levels%20of%20Perfluorinated%20Compounds%20in%20New%20Jersey%20Fish,%20Surface%20Water,%20and%20Sediment.pdf

The Division of Science, Research, and Environmental Health (DSREH) within the New Jersey Department of Environmental Protection performed an initial assessment of 13 PFAS, all of which are perfluorinated compounds (PFC), at 11 waterways across the state. Fourteen surface-water and sediment samples and 94 fish-tissue samples were collected at sites along these waterways. The sites were selected based on their proximity to potential sources of PFAS and their likelihood of being used for recreational and fishing purposes.

New York

"Per- and Polyfluorinated Substances (PFAS)"

A web page published by New York State's Department of Environmental Conservation (DEC) on its website.

URL: https://www.dec.ny.gov/chemical/108831.html

Statewide PFAS Survey

DEC surveyed select businesses, fire departments, fire-training centers, bulk-storage facilities, airports, and Department of Defense (DoD) facilities from June to September 2016. The responses to the survey have helped to determine if these entities have used or stored PFOA/PFOS. The results have provided essential information to DEC and to the Water Quality Rapid Response Team so that they can further investigate additional areas for potential contamination. The results of this survey will be updated periodically as additional responses are received.

State Firefighting Foam Collection Efforts

Through funding prioritized by Governor Andrew Cuomo in the Environmental Protection Fund, DEC has worked with the Division of Homeland Security and Emergency Services to launch a collection program for the removal and appropriate disposal of firefighting foam containing perfluorinated compounds. Through the $600,000 investment, DEC is working with municipal fire and emergency response departments across the state to dispose of the contaminated foam. As of the end of 2017, more than 20,000 gallons of contaminated foam have been collected and properly disposed; the collection is ongoing.

Vermont

"Perfluoroalkyl Substances (PFAS) Contamination Status Report" (July 2018)

URL:
http://dec.vermont.gov/sites/dec/files/documents/PFAS%20Sampling%20Report%207.10.18%20FINAL.pdf

In February 2016, Vermont's Department of Environmental Conservation (DEC) discovered a contamination problem in Bennington of perfluoroalkyl substances (PFAS) from a former Teflon-coating factory located in North Bennington. Since that first discovery, the DEC has investigated numerous sources of PFAS using a strategic sampling strategy that is updated and adapted based on the latest scientific research. This report provides an overview of the findings of this work and provides a look into additional work needed in the future.

Michigan

"PFAS Response, Taking Action to Protect the Public's Water"

Michigan PFAS Action Response Team (MPART)

URL: https://www.michigan.gov/pfasresponse/

In 2017, the Michigan PFAS Action Response Team (MPART) pulled together agencies representing health, environment, and other branches of state government to investigate the sources and location of PFAS contamination in the state, take actions to protect drinking water, and keep the public informed. The state is working

1) to better understand how PFAS may affect people's health;

2) to identify locations where PFAS may be present as a contaminant by testing drinking water from all community water supplies and a selection of groundwater, lakes and streams, soil, sediment, wastewater, and PFAS foam that can accumulate at lakes and rivers;

3) to provide a map of confirmed detections of PFOA and PFOS in groundwater;

4) to test deer and fish for PFAS and issue "do not eat" advisories as appropriate;

5) and to work with the fire service community to identify the amount of PFAS foam in use, it's training and emergency storage protocols, and other best-practice procedures in order to develop statewide solutions to dispose of the foam properly and prevent further contamination.

Australia

"Inquiry into the management of per- and polyfluoroalkyl substances (PFAS) contamination in and around Defence bases"

A report from the Joint Standing Committee on Foreign Affairs, Defence and Trade, the Parliament of Australia

URL:
https://www.aph.gov.au/Parliamentary_Business/Committees/Joint/Foreign_Affairs_Defence_and_Trade/InquiryintoPFAS

On 30 May 2018, the Joint Standing Committee on Foreign Affairs, Defence and Trade adopted an inquiry referred by the Australian Senate, asking the committee to inquire into and report on the management of per- and polyfluoroalkyl substances (PFAS) contamination in and around Australian Defence bases.

The following is an extract from the report:

> Terms of Reference
> The Committee shall inquire into the Commonwealth Government's management of per- and polyfluoroalkyl substances (PFAS) contamination in and around Defence bases, with particular reference to:
> a) the extent of contamination in and around Defence bases, including water, soil, other natural assets and built structures;
> b) the response of, and coordination between, agencies of the Commonwealth Government, including, but not limited to, the Department of Prime Minister and Cabinet, the Department of Health, the Department of the Environment and Energy, the Department of Defence and the Australian Defence Force;
> c) communication and coordination with state and territory governments, local councils, affected local communities and businesses, and other interested stakeholders;
> d) the adequacy of health advice and testing of current and former defence and civilian personnel and members of the public exposed in and around Defence bases identified as potentially affected by contamination;
> e) the adequacy of Commonwealth and state and territory government environmental and human health standards and legislation, and any other relevant legislation;
> f) remediation works at the bases; and
> g) what consideration has been given to understanding and addressing any financial impact to affected businesses and individuals.

Australian Government PFAS Website

URL: https://www.pfas.gov.au/

This website provides easy access to information on per- and polyfluoroalkyl substances (PFAS) and PFAS contamination for a wide range of interested audiences. It provides links to PFAS information pages on Commonwealth and State/Territory government agency websites, as well as links to relevant international sites. PFAS-specific guidance materials can also be accessed on this site. Follow the links to search for PFAS information by audience, location, or topic.

"Expert Health Panel for PFAS Report" (April 2018)

URL: http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-expert-panel.htm

The Australian Government established the Expert Health Panel for PFAS to advise on the potential health impacts associated with PFAS exposure and to identify priority areas for further research.

New Zealand

URL: http://www.mfe.govt.nz/land/pfas-and-poly-fluoroalkyl-substances/pfospfoa-nz

According to New Zealand's Ministry for the Environment, no importation, manufacture, or use of PFOS compounds is permitted, with the only exception being when it is for laboratory use. Furthermore, The New Zealand Defence Force has been advised by its suppliers that since 2002 they have not supplied to NZDF any foam products containing PFOS or PFOA above trace levels.

Fire and Emergency NZ (FENZ) has had the bulk of its Class B foam stocks chemically analysed, and has confirmed that none of these products contain any PFOS or PFOA.

FENZ is taking a precautionary approach and instructing its personnel not to use the small amount of type of Class B foams that has not been tested as at this stage they can’t be completely assured that they don’t contain PFOS or PFOA.

D.3 Industry

PERF (Petroleum Environmental Research Forum)

URL: http://perf.org/projects/

Project 2016-05

Below is an extract from the project documentation:

> A mixture of Per- and Poly-fluorinated Alkylated Substances (PFAS) are found in aqueous film-forming foams (AFFF) used for firefighting. Some of the long-chain PFAS and some of their degradation products are highly persistent in the environment, bioaccumulative in wildlife and humans, and have been linked to environmental and human health impacts. The nature of oil and gas operations necessitates the use of AFFFs to combat liquid hydrocarbon fires and use of AFFFs in drills and incidents may result in input of PFAS into the environment. The costs and feasibility of long-chain AFFF stockpile replacement are unclear and must be balanced with the risk reduction realized from switching to short-chain AFFFs or fluorine-free foam. While scientific studies support that short-chain PFAS AFFFs are less bioaccumulative and toxic, a recent compilation of these data is needed to address uncertainty in how much short-chain PFAS AFFFs or fluorine-free foam reduces H&E risks.
>
> This project aims to capture the state of knowledge of the fate, transport, and effects of short-chain PFAS-based AFFFs and fluorine-free firefighting foams and identify limitations of and data gaps in the current studies or data sets. This project will help to address uncertainties regarding human health and environmental hazards associated with long-chain PFAS foam alternatives, inform future research opportunities, support advocacy for effective fire response tools, and inform risk-based decision-making on foam replacement and management.

Project status (April 2018): A contract for this work was put out for bid in May 2018. The project manager reported that the contract includes an alternatives assessment for fluorine-containing and fluorine-free foams. The project may use GreenScreen® assessments and may use the IC2 Alternatives Assessment methodology. However, the final comparisons will likely be based on risk assessment calculations. The current plan is to include foam ingredient chemicals (as delivered) and their final degradates in the chemical hazard assessment.

LASTFIRE Project, United Kingdom

URL: http://www.lastfire.co.uk/default.aspx?ReturnUrl=%2f

On behalf of a consortium of 16 oil companies, a project was initiated in the late 1990s to review the risks associated with large diameter (greater than 40 m) open-top, floating-roof storage tanks. The project was known as the LASTFIRE Project ("LAST" meaning "Large Atmospheric Storage Tanks"). The project was initiated due to the oil and petrochemical industries recognition that the fire hazards associated with large-diameter, open-top, floating-roof tanks were insufficiently understood to be able to develop fully justified site specific fire response and risk reduction policies

Research Paper: "Foam Concentrate Usage and Options" (October 2016)

URL: http://www.lastfire.co.uk/uploads/Foam%20Position%20Paper%20Issue%202%20Oct%202016%20s.pdf

LASTFIRE Foam Summit: 17-18 October 2017 (Budapest, Hungary)

The LASTFIRE Foam Summit follows the "Cradle-to-Grave" approach used in the recently published LASTFIRE Foam Assurance Guidance and Questionnaire. It included speakers from around the world. Presentations are available here: http://www.lastfire.org.uk/refmatpapers.aspx

Firefighting Foam Summit and Fire Extinguishing Tests: October 2018 (Dallas/Fort Worth Airport, TX)

An international event organized by LASTFIRE, Arcadis, and DFW Airport to review the current situation related to selection, use, and management of firefighting foam.

Dallas/Fort Worth Fire Training Research Center

URL: https://www.dfwairport.com/firetraining/#slide-1
This center has presented results on the performance of fluorine-free foams. They may be a good source of information on performance testing and may have experience with fluorine-free foam performance.

D.4 Independent Organizations

Clean Production Action

Firefighting Foam – Identify, prioritize, and assess alternatives with GreenScreen Certified™

The following is from the Clean Production Action website (https://www.cleanproduction.org/):

> Clean Production Action is collaborating closely with Toxic-Free Future and King County Local Hazardous Waste Management Program to reduce exposure to PFAS in firefighting foam in Washington State. Our focus is to educate and align stakeholders on the need to ensure PFAS-free products are also safer and not regrettable substitutes, to create market pressures for manufacturers of PFAS-free products to use hazard assessment to evaluate ingredients, and to create a list of preferred PFAS-free products using GreenScreen Certified™. For more information, contact Clean Production Action at greenscreen@cleanproduction.org.

Toxic-Free Future, State of Washington

URL: https://toxicfreefuture.org/science/chemicals-of-concern/perfluorinated-chemicals-pfcs/
Toxic-Free Future works to eliminate PFAS in AFFF and food packaging in the State of Washington.

Contact: Erika Schreder | Science Director, eschreder@toxicfreefuture.org, 206-632-1545 x 119 Toxicfreefuture.org

Green Science Policy Institute

The Green Science Policy Institute hosts monthly PFAS conference calls. Below are relevant publications.

- "PFAS in Drinking Water: The Need for a Coordinated Strategy" (URL: http://greensciencepolicy.org/pfas-statement/)
- "Consumers' Guide to Highly Fluorinated Chemicals" (URL: http://greensciencepolicy.org/highly-fluorinated-chemicals/)

Appendix F: Detailed Summaries of Firefighting-Foam Research

The National Academies of Sciences publication *A Framework to Guide Selection of Chemical Alternatives* and the IC2's *Alternatives Assessment Guide* were consulted to determine the point in the alternatives assessment process at which the research papers collected below are most useful. A summary of each paper is included. Papers are listed alphabetically by title within the applicable framework step, the title and location where the work took place and/or the authors' affiliations is included, and a link to the paper is provided.

1. Identify Chemical of Concern

"Identification of Novel Fluorochemicals in AFFF Used by the U.S. Military,"

URL: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3390017/

Fast-atom-bombardment mass spectrometry (FAB-MS) and high-resolution quadrupole-time-of-flight mass spectrometry (QTOF-MS) were combined to elucidate chemical formulas for the fluorochemicals in AFFF mixtures used by the U.S. military. Structures were assigned along with patent-based information. Sample collection and analysis were focused on AFFF that have been designated as certified for U.S. military use. Ten different fluorochemical classes were identified in the seven military-certified AFFF formulations, and include anionic, cationic, and zwitterionic surfactants with perfluoroalkyl chain lengths ranging from 4 to 12. The environmental implications are discussed and research needs are identified.

2. Scoping and Problem Formulation

"Preliminary Assessment Aqueous Film-Forming Foam Use Portland International Airport Portland," Oregon

URL: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3390017/

Study performed to determine the history of AFFF at an airport and other high-use areas. Provides detailed insight into operations and history at the airport; this may be helpful with identifying stakeholders and understanding performance requirements

"Queensland Firefighting Foam Survey—Results Summary," Australia

URL: https://environment.des.qld.gov.au/assets/documents/pollution/management/incidents/firefighting-foam-survey-summary.pdf

Recent survey of foam uses in the Australian state of Queensland. Type of foam and industry groups are identified. Useful for identifying industry groups for outreach and potential stakeholders.

- Industries most likely to use and store foam are bulk fuel and chemical storage.

"Use and Potential Impacts of AFFF Containing PFAS at Airports," U.S. Transportation Research Board

URL: https://www.nap.edu/read/24800/chapter/6

- Metal-plating operations utilize fluorinated compounds and are considered essential. It is possible they contribute to contamination of areas.
- Recommended for future research: Alternatives to AFFF containing PFAS, disposal methods, replacing AFFF in existing systems, environmental standards for AFFF, evaluation of existing separation/treatment facilities for processing wastewater impacted by PFASs, understanding how firefighting can be optimized, broadly applicable analytical methods, environmental and human-health risks associated with short-chain PFAS in AFFF, feasible cost-effective remediation techniques and/or approaches.

3. Identify Potential Alternatives

"Fire Testing a New Fluorine-Free AFFF Based on a Novel Class of Environmentally Sound High-Performance Siloxane Surfactants," Germany

URL: http://iafss.org/publications/fss/11/1261/view/fss_11-1261.pdf

A new family of carbohydrate siloxane surfactants was synthesized and successfully tested for film-forming capabilities.

- May be possible to produce a fluorine-free AFFF for the military—relevant fuels are based on siloxane surfactants.

- A comparison of commercial firefighting foam agents with the experimental siloxane surfactant blend and blind tests proves that the water film significantly promotes the extinguishing performance in terms of extinction times and burnback process. It is particularly noticeable that the extinguishing performance of the experimental siloxane blend is only surpassed by the fluorine-containing AFFF, although its composition is net yet optimized. Conversely, the fluorine-free Class B foams clearly perform worse. For the future, the drainage of the siloxane-containing foam should be adjusted to the behavior of the fluorinated foam to optimize the burnback characteristics of the foam.

“Fire Testing of Experimental Siloxane-Based AFFF: Results From New Experiments,” Germany

URL: https://www.nfpa.org/-/media/Files/News-and-Research/Resources/Research-Foundation/Symposia/2015-SUPDET/2015-papers/SUPDET2015HetzerAbstract.ashx?la=en

More than 250 siloxane and carbosilane surfactants were synthesized and tested as possible film-formers for fluorine-free foams. The surfactant T-C3-Malt was chosen for a fire test because of its film-forming ability and foaming behavior. Five foam solutions were mixed and four application rates of each foam were tested.

- The series of fire tests shows that the rising of the siloxane surfactant concentration strongly reduces the fire-extinguishing times on F-34 fuel. In comparison with commercially available fluorine-free Class B foams and fluorinated foams, according to the German Armed Forces technical specification TL 4210-0112, the experimental siloxane-based aqueous film-forming foams clearly surpass the fluorine-free Class B foams and reach nearly the extinguishing performance of the fluorinated foams in small-scale fire tests.
- Conducted experiments show the ability of siloxane surfactants to act as an alternative film-forming compound for fluorine-free high-performance firefighting foams for pool fires.

“Fluorine-Free Firefighting Agents and Methods,” U.S. Patent Application US2005000119, issued 2006

URL: https://patents.google.com/patent/US20050001197A1/en?q=~patent%2fUS9687686B2&page=1

A foam concentrate comprising water and a high-molecular-weight acidic polymer (HMWAP), and a coordinating salt.

“Fluorine-Free Firefighting Agents and Methods,” U.S. Patent Application US20050001197A1, issued 2006

URL: https://patents.google.com/patent/US20050001197A1/en

Kirtland Clark (original assignee: Chemguard, current assignee: Tyco Fire and Security GmbH)

The concentrate is formed from water, a high-molecular-weight acidic polymer (HMWAP), and a salt.

“Silica Foams for Fire Prevention and Fire Fighting,” Russia

URL: https://pubs.acs.org/doi/abs/10.1021/acsami.5b08653

Detailed description of the physicochemical processes of silica-foam formation at the molecular level and functional comparison with current fire-extinguishing and firefighting agents.

- As a result of fire-extinguishing tests, it is shown that the extinguishing efficiency exhibited by silica-based sol−gel foams is almost 50 times higher than that for ordinary water, and 15 times better than that for state-of-the-art, firefighting-agent aqueous film-forming foam. The biodegradation index determined by the time of the induction period was only 3 d, while, even for conventional foaming agents, this index is several times higher.

“Silicon-Containing Organic Acid Derivatives as Environmentally Friendly AFFF Extinguishing Agent,” U.S. Patent Application US20170259099A1, pending 2015

URL: https://patents.google.com/patent/DE102014112851A1/en

A firefighting foam concentrate with a first surfactant that comprises an acid group and/or a deprotonated acid group and an oligosilane unit and/or oligosiloxane unit.

“Siloxane-Containing Fire Extinguishing Foam,” U.S. Patent 9,687,686, issued June 27, 2017, for fluorine-free foam

URL: https://patents.google.com/patent/US9687686B2/en

Professor Dirk Blunk at the University of Cologne (Germany) has multiple patents on alternatives. It is a carbohydrate-containing siloxane surfactant.

"Survey of Fire-Fighting Foam," Swedish Chemicals Agency (KEMI)

URL: https://www.kemi.se/global/pm/2015/pm-5-15-survey-of-fire-fighting-foam.pdf

Summary of foam use in Sweden. Authors reached out to manufacturers for information on their products. List of foams and their ingredients are provided as an appendix.

"The Phase-out of Perfluorooctane Sulfonate (PFOS) and the Global Future of Aqueous Film-Forming Foam," India

URL: http://pubs.sciepub.com/ces/2/1/3/

High-level discussion of the history of fluorinated foams with a brief interlude about where the industry is headed with telomere-based foams.

- Foams are now telomere-based, which has displaced electrochemical fluorination as the primary synthesis method. Telomer surfactants are generated via telomerisation. Telomers are typically shorter in chain length (< C6) and are perfluorinated as opposed to polyfluorinated.

4. Assess Human Health Hazards

"Environmental Management of Firefighting Foam Policy - Explanatory Notes (Revision 2)," Australia

URL: https://www.qld.gov.au/__data/assets/pdf_file/0034/68776/firefighting-foam-policy-notes.pdf

Comprehensive study on the distinctions between different types and aspects of fluorinated foams. Focus on impacts of firefighting foams, including ecotoxicity, and human-health concerns, treatment and disposal of foams, and use issues.

"What Properties Matter in Fire-Fighting Foams?" Australia and the United States

URL: https://www.solbergfoam.com/getattachment/3fe1d44d-3b44-4714-89f4-4af37e381b5b/WP-WHAT-PROPERTIES-MATTER-IN-FIRE-FIGHTING-FOAMS.aspx

Describes important properties in firefighting foams, identifies a number of standards that firefighting foams must follow. Provides a comprehensive list of each foam's various properties, why standards have chosen to address them, the reason behind certain values, and the most concerning physical properties of foams. Additional explanations provide insight into why certain values and properties were chosen. Properties of bubbles are explored and their effect on foams discussed.

- Concerns were raised that all PFAS decompose to perfluorooctanesulphonic acid (PFOSH), which binds to blood and buildup in the gallbladder and liver. This may be due to the body mistaking these compounds for bile acids. No adverse effects have been reported.
- PFOA, specifically ammonium salt, was concluded by EPA to be weakly carcinogenic.

5. Assess Ecotoxicity

"Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater," United States

URL: https://pubs.acs.org/doi/abs/10.1021/acs.est.6b05843?src=recsys

An in-depth analysis on fluorinated compounds found in contaminated groundwater sites using mass spectroscopy as the primary characterization method.

"Discovery and Implications of C_2 and C_3 Perfluoroalkyl Sulfonates in Aqueous Film-Forming Foams and Groundwater," United States

URL: https://pubs.acs.org/doi/abs/10.1021/acs.estlett.5b00049

Evidence showed that the short chain compounds in 3M's foams have persisted in the environment for about 15 years. Paper recommends PFEtS and PFPrS be included among the PFASs monitored in groundwater potentially impacted by AFFFs and other PFASs sources.

"Environmental Management of Firefighting Foam Policy - Explanatory Notes (Revision 2)," Australia

URL: https://www.qld.gov.au/__data/assets/pdf_file/0034/68776/firefighting-foam-policy-notes.pdf

Comprehensive study on the distinctions between different types and aspects of fluorinated foams. Focuses on impacts of firefighting foams, including ecotoxicity and human-health concerns, treatment and disposal of foams, and use issues.

“Historical Usage of Aqueous Film-Forming Foam: A Case Study of the Widespread Distribution of Perfluoroalkyl Acids From a Military Airport to Groundwater, Lakes, Soils, and Fish,” Sweden

URL: https://www.sciencedirect.com/science/article/pii/S0045653514010650?via%3Dihub

Transport of fluorinated compounds from extinguishing sites through concrete to groundwater and fish.

“Foam Concentrate Usage and Options,” LASTFIRE Group

URL: http://www.lastfire.co.uk/uploads/Foam%20Position%20Paper%20Issue%202%20Oct%202016%20s.pdf

Practicality and performance of fluorine-free foams as compared to fluorinated counterparts, including anecdotal evidence of performance with fluorine-free foams.

- List of environmental data that should be included when assessing a foam: dissolved oxygen, BOD (biological oxygen demand), persistence in the environment, bioaccumulation, toxicity, COD (chemical oxygen demand), and aquatic toxicity.

“Perfluorinated Surfactants and the Environmental Implications of Their Use in Fire-Fighting Foams,” United States

URL: https://pubs.acs.org/doi/abs/10.1021/es991359u

Technical overview of the potential impact of AFFF on the environment. Published in 2000, so while it provides some good points, it may be outdated.

“Perfluoroalkyl Substances in a Firefighting Training Ground, Distribution, and Potential Future Release,” Australia

URL: https://www.sciencedirect.com/science/article/pii/S0304389415001958?via%3Dihub

Analysis of long- and short-chain fluorinated compounds traveling through and retaining in concrete washpads in Australia. Shorter chain compounds move more easily through the concrete and were found throughout the vertical column. Long-chain compounds were found exclusively at the surface layer. This may imply that shorter chain compounds are more mobile and can impact groundwater more readily.

“The Search for Alternative Aqueous Film-Forming Foams (AFFF) With a Low Environmental Impact: Physiological and Transcriptomic Effects of Two Forafac® Fluorosurfactants in Turbot,” *Aquatic Toxicology* (August 2011)

URL: https://www.sciencedirect.com/science/article/pii/S0166445X1100110X?via%3Dihub

An in-depth study of two specific foams and their toxicity to fish. One foam consists of C6 and C8 fluorochemicals and the other consists of C6, C8, C10, and C12 fluorochemicals.

“Use and Potential Impacts of AFFF Containing PFAS at Airports,” U.S. Transportation Research Board

URL: https://www.nap.edu/read/24800/chapter/6

Comprehensive look at foam use in airports. Survey of 167 airports across the US & Canada focused on life cycle of foams and legacy impacts.

- Two-thirds of the responding North American airports indicated that AFFF discharged during testing is disposed of onto the ground. The remaining third of respondents discharge AFFF into an engineered containment system. For the one-third of respondents who used engineered containment systems, the type of system most widely used was a small or non-permanent vessel, and the next most widely used system was testing in a designated area such as a containment basin or training pit.

6. Life-Cycle Thinking

Funding Provided by the NYS Department of Environmental Conservation

“Use and Potential Impacts of AFFF-Containing PFAS at Airports,” U.S. Transportation Research Board
URL: https://www.nap.edu/read/24800/chapter/6

Comprehensive look at foam use in airports. Survey of 167 airports across the United States and Canada that is focused on the life cycle of foams and legacy impacts.

7. Performance Assessment

“The Extinguishing Performance of Experimental Siloxane-Based AFFF,” Germany
URL:
https://www.researchgate.net/profile/Ralf_Hetzer/publication/305033141_The_Extinguishing_Performance_of_Experimental_Siloxane-Based_AFFF/links/577f7ad108ae9485a43983ca/The-Extinguishing-Performance-of-Experimental-Siloxane-Based-AFFF

Siloxane-based foam is tested against the German military performance standard, and performs as well as fluorinated foams and better than fluorine-free foams on F-34 fires.

- Fluorine-free siloxane based foam can be achieved for military relevant fuels on the base of siloxane surfactant SLB.
- The siloxane-based foams exhibit an extinguishing performance similar to fluorinated foam according to TL 4210-0112 (German military specification) and significantly outperform the fluorine-free foams on fires of the NATO standard fuel F-34.
- Additional laboratory and application tests demonstrate that the experimental siloxane-based foam concentrate is surprisingly near to a commercially viable foam concentrate. Furthermore, it already matches the requirements of the German military technical specification in many aspects.

“Extinguishment and Burnback Tests of Fluorinated and Fluorine-Free Firefighting Foams With and Without Film Formation,” U.S. National Fire Protection Association (NFPA)
The fire extinguishment and burnback performance of three foams (two fluorinated MIL-SPEC qualified foams and one fluorine-free foam) were tested on four low-flash-point fuels with different surface tensions. This paper is often cited in articles referring to the limitations of fluorine-free foams.
- AFFFs did not perform any better than fluorine-free foam when film formation was not possible.
- Fluorine-free foams behave more consistently than AFFF.

“The Future of Aqueous Film-Forming Foam (AFFF): Performance Parameters and Requirements,” U.S. Navy Technology Center for Safety and Survivability
URL: https://www.nist.gov/sites/default/files/documents/el/fire_research/R0201327.pdf

Provides insight into the reasoning behind MIL-F-24385F. Specifically, it explains how AFFF operates and it establishes the role of fluorinated carbons in AFFF. It also describes the challenges of MIL-SPEC, outlines the surface tension requirements of MIL-SPEC, and summarizes the issues many have raised concerning MIL-SPEC’s use of equilibrium surface tension values.

“Influence of Fuel on Foam Degradation for Fluorinated and Fluorine-Free Foams,” U.S. Naval Research Laboratory
URL: https://www.sciencedirect.com/science/article/pii/S0927775717302169

Theoretical discussion on how foam is influenced by various parameters like heat and bubble size.
- Mixed surfactants are better at slowing degradation than individual surfactants.
  - ○ Smaller chain hydrocarbons also contribute to faster degradation.
  - ○ Heat can also contribute due to increased evaporation and expansion of gas inside of bubbles causing ruptures and liquid drainage.
  - Foam lifetime decreases as temperature of the fuel increases. Severe enough to change the scale of degradation from hours at room temperature to minutes at elevated (50 °C) temperatures. This is due to increased fuel vapors at the interface.
    - ○ At 50 ° C, RF6 degrades in three minutes. Buckey degrades in 35 minutes.

“LASTFIRE Large Atmospheric Storage Tank Fires, Foam Concentrate Usage, and Options,” LASTFIRE Group

URL: http://www.lastfire.co.uk/uploads/Foam%20Position%20Paper%20Issue%202%20Oct%202016%20s.pdf

Practicality and performance of fluorine-free foams as compared to fluorinated counterparts, including anecdotal evidence of performance with fluorine-free foams.

- Performance testing shows that C6 products have not performed as well as C8. One manufacturer reported that changing to a C6 formulation will result in reduced performance or higher cost, and concludes no “C6-based or FF formulations have been able to achieve the same levels of extinguishing performance demonstrated by previously proven high-quality concentrates for tank-fire application.”

“Measuring Fuel Transport Through Fluorocarbon and Fluorine-Free Firefighting Foams,” U.S. Naval Research Laboratory

URL: https://www.sciencedirect.com/science/article/pii/S0379711217301352?via%3Dihub

Focuses on the major factors affecting fuel transfer in firefighting foams. Provides good insight into characteristics of interest when it comes to suppressing fuel transfer and, therefore, potential flash fires.

- Fluorine-free RF6 (Solberg) forms larger bubbles than Buckeye 3% (Buckeye Fire Equipment) and has a longer drainage time. May contribute to fuel flux and ignition.
- Fluorinated foams had lower fuel fluxes consistently across several different fuels as compared to RF6.
    - Fluorosurfactants are likely the cause, as they contain highly oleophobic aspects that attempt to reject the fuel as it attempts to transfer through the barriers, which slows down flux. RF6 does not contain oleophobic surfactants and therefore has less discouraging power.
- Experiments with iso-octane indicate that the foam layer may be more important than the aqueous film to fuel flux. This is likely due to the many bubbles present in the foam and how difficult it would be for fuel to transfer through so many mediums and surfaces.

“Preliminary Assessment: Aqueous Film-Forming Foam Use Portland International Airport,” Portland, Oregon

URL: https://www.deq.state.or.us/Webdocs/Controls/Output/PdfHandler.ashx?p=4079b1d7-f8b6-4343-b701-e739287b8357.pdf&s=Preliminary%20Assessment%20Aqueous%20Film-Forming%20Foam%20Use%20PDX%2020170803.pdf

Summarizes the history of AFFF at an airport and other high-use areas. Provides detailed insight into operations and history at the airport. It may be a helpful resource for identifying stakeholders and building an understanding of performance requirements.

“Sealability Properties of Fluorine-Free Fire-Fighting Foams,” *Fire Technology* (September 2008)

URL: https://link.springer.com/article/10.1007/s10694-007-0030-8

Comparison of three synthetic foams without fluorine and AFFF-vapor sealability performance utilizing Australian Defense Force Specification (DEF(AUST)) 5706. Provides strong insight into concerns with vapor suppression and briefly discusses tests with respect to actual practices. Useful for discussing vapor suppression in foams and their purpose to firefighting foams.

- In performance testing, Fluorine-free RF6 (Solberg) struggled to contain vapors well as it does not form a film. AFFF consistently outperformed all other foams in all areas. RF6 consistently came in second in all areas. Formulations A and B (both fluorine free) were erratic and always came in third/fourth in all areas.
    - Actual practices in firefighting have foam reapplied frequently and the performance of both the AFFF and RF6 increased dramatically when following these guidelines. It is suggested that in a practical scenario, RF6 would perform adequately.

“Siloxane-Based AFFF: Testing of Experimental Foam Concentrates,” Bundeswehr Research Institute for Protective Technologies and NBC-Protection (WIS), Germany

URL: https://www.nfpa.org/-/media/Files/News-and-Research/Resources/Research-Foundation/Symposia/2016-SUPDET/2016-Papers/SUPDET2016Hetzer.ashx?la=en

- Performance and toxicological parameters of a siloxane-based foam (consisting of 180 g/kg Glucopon 215 CS UP, 150 g/kg siloxane surfactant 1, 500 g/kg 2-[2-Butoxyethoxy] ethanol and 170 g/kg solvent) compared to fluorinated foam.
- Performance and toxicological parameters of a siloxane-based foam (consisting of 180 g/kg Glucopon 215 CS UP, 150 g/kg siloxane surfactant 1, 500 g/kg 2-(2-Butoxyethoxy)ethanol) show:
    - An extinguishing performance that significantly surpasses the commercial fluorine-free foams and nearly meets the performance of the fluorinated foams in the fire suppression tests with the NATO standard fuel F-34.
    - The viscosity and density of the 1% siloxane-based foam concentrate are acceptable in a temperature range between -15 °C and 60 °C
    - The toxicological behavior of the siloxane-based experimental foam concentrate is acceptable.
    - Siloxane-based fluorine-free foams are easily manufactured and perform significantly better on F-34 than the non-aqueous film form class-B-foam without persistent ingredients.

"What Properties Matter in Fire-Fighting Foams?" National Research Institute of Fire and Disaster

URL: https://www.solbergfoam.com/getattachment/3fe1d44d-3b44-4714-89f4-4af37e381b5b/WP-WHAT-PROPERTIES-MATTER-IN-FIRE-FIGHTING-FOAMS.aspx

Describes important properties in firefighting foams. Identifies a number of standards firefighting foams must follow. Also provides a list that outlines the properties of foams, why specific standards were chosen, the reasoning behind certain values, and the physical properties of foams that cause the most concern. Additional explanations provide further insight into why certain values and properties are included when creating standards. Properties of bubbles are explored and their effect on foams discussed.

- Fluorosurfactants are useful because they exhibit hydrophilic heads and hydrophobic tails. This is a unique property that makes forming a film possible.

<END>

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ALTERNATIVES TO PFAS-COATED FOOD PACKAGING

Nonstick chemicals known as per- and poly-fluorinated alkyl substances (PFAS) are commonly used in disposable food packaging and food service ware as an oil and grease barrier. Concerns about their hazards are creating demand among grocery stores and government, health care, educational and other institutional purchasers for safer alternatives.

Food service ware products and product categories that may contain PFAS include:

- bowls
- plates
- clamshells/take-out containers
- food trays/boats
- bags such as for rotisserie chicken
- straws
- boxes such as for pizza, pastry
- wrappers and liners such as muffin papers, cookie bags, hot or cold sandwich bags, parchment paper, self-serve sheets

Food service ware products and product categories that typically do NOT contain PFAS include:

- cups (hot and cold)
- cutlery
- stirrers
- coffee sleeves
- napkins

ALTERNATIVES ARE AVAILABLE

Single-use disposable food packaging and service ware are available without PFAS, including uncoated paper products, products made with materials other than paper, and paper products treated with coatings other than PFAS. The table below summarizes the product categories of single-use compostable food service ware that typically contain PFAS and the PFAS-free alternative materials and/or coatings available.

Product Category	Alternates to Paper	Alternate Treatments
Bowls	PLA (compostable plastic) Bamboo Palm leaf	None (Uncoated) PLA Clay Soak Proof Shield™
Plates	Bamboo Palm Leaf	None (Uncoated) Soak Proof Shield™ Clay
Clamshells & Take out Containers	PLA	PLA Enshield®
Food trays/boats	PLA	None (Uncoated) Clay
Boxes		Bio-wax
Wrappers and Liners		Bio-wax

COMPOSTABLE PFAS-FREE ALTERNATIVES

Below is a description of compostable PFAS-free alternatives and associated manufacturers and brands. Some products from these brands may contain PFAS, so it is important for purchasers to specify PFAS-free.

Uncoated Products: an alternate mechanical process can make paper and paperboard grease-resistant by compressing the fibers—currently made by Nordic Paper. Another manufacturer of uncoated paper plates is AJM Packaging Corporation.

Alternative Materials: Compostable materials other than paper are used to make oil and grease resistant food service ware.

- Polylactic Acid (PLA) is a compostable plastic typically made from corn—made by a number of manufacturers including Natureworks under the Ingeo® brand and used by Eco-Products , Greensafe Products, GrowPlastics, and World Centric®. Products include bowls, clamshells, take-out containers and lids, deli containers, cutlery, and portion cups.
- Bamboo—Bambu® manufactures disposable plates and bowls from thin sheets of bamboo.
- Palm Leaf produced by Resposable and by BioMass Packaging under the Leafware® brand.

Alternative Treatments: Paper coated with PLA, silicone, clay, and other proprietary-branded coatings and treatments are used to impart oil and grease resistance to disposable food service ware.

- PLA—PLA coated paperboard soup bowls and take-out containers have been produced by: Practiv's Earthchoice, Graphic Packaging International's Ecotainer®, Eco-Products® World Art ™, PrimeLink Solutions' PrimeWare®, Karat, Vegware, and World Centric®.
- Clay—Dart Container Corporation manufactures clay-coated paper plates under the brand Bare® By Solo® Eco-Forward®. Eco-Products and Monogram also make clay coated food boats.
- Bio-wax—Bio-based wax coatings are produced by Clondakin Group under the Ecowax® brand and by Paramelt under the Paraflex NoWax™ brand for a variety of food contact applications including bags, wraps, and boxes.
- Proprietary branded coatings of unknown hazard profile:
    - Soak Proof Shield™—Georgia-Pacific manufactures a line of paper plates and bowls under the Dixie® brand coated with Soak Proof Shield™, an acrylic-based coating that does not contain silicone.
    - Enshield®— West Rock produces oil and grease resistant paperboard coated with Enshield® for a variety of food service applications including take-out, bakery, and frozen foods.
    - Unknown – Brands of plates and bowls with unknown coating or possibly no coating include Cheeky, Target's store brand Up & Up, and Walgreen's store brand Nice!.

Durable and reusable food service ware is preferred over single use disposable materials to reduce consumption of materials and waste generation. Compostable materials need a dedicated collection system and industrial composting facility to adequately close the materials loop. Most petroleum based single use plastics are not recycled. A lifecycle perspective of material type and waste infrastructure should also be considered when addressing the toxicity profile of materials.

MORE ALTERNATIVES ARE COMING

Manufacturers are responding to the market demand for fluorine-free compostable food service ware products from large-scale purchasers e.g., academic institutions, state governments, the education sector and health care systems. Manufacturers are actively working on non-fluorinated alternatives and new products are expected to be on the market within the coming year.

The following organizations contributed research and testing results that helped inform this fact sheet: Center for Environmental Health, Responsible Purchasing Network, and San Francisco Department of the Environment.

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OR DEQ Roadmap: Evaluating Alternatives to Food Packaging Materials Containing Per- or Poly-fluorinated Substances (PFASs)

Northwest Green Chemistry

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Abbreviations

AA	Alternatives Assessment
ABA	Australasian Bioplastics Association
AS	Australian Standard
ASTM	American Society for Testing and Materials
BPI	Biodegradable Products Institute
CBI	Confidential business information
CEH	Center for Environmental Health
CHA	Chemical hazard assessment
CIC	Combustion Ion Chromatography
C*n*	PFASs with *n* carbon-fluorine bonds, e.g. C6 refers to PFAS substances with 6 C-F bonds
DWR	Durable water repellent
FPI	Foodservice Packaging Institute
GS	GreenScreen for Safer Chemicals
GS LT	GreenScreen List Translator
HPLC	High performance liquid chromatography
IC2	Interstate Chemicals Clearinghouse
ISO	International Organization for Standardization
LC	Liquid chromatography
LC-MS/MS	Liquid chromatography with tandem mass spectrometry
LCA	Life cycle assessment
LCT	Life cycle thinking
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectrometry
NDA	Non-disclosure agreement
NGC	Northwest Green Chemistry
NMR	Nuclear magnetic resonance
OR DEQ	Oregon Department of Environmental Quality
PLA	Polylactic acid
PS	Polystyrene
PET	Polyethylene terephthalate
PFAA	Perfluoroalkyl acid
PFASs	Per- and poly-fluorinated alkyl substances
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PIGE	Particle-Induced Gamma Ray Emission
PP	Polypropylene
PPE	Personal protective equipment
SCIL	Safer Chemicals Ingredients List

TAPPI	Technical Association of the Pulp and Paper Industry
US EPA	United States Environmental Protection Agency
WA DOE	Washington State Department of Ecology

Executive Summary

This report provides a roadmap for conducting a full alternatives assessment (AA) for food packaging that is free of per- and poly-fluoroalkyl substances (PFASs) and identifies some currently available alternatives (see supplemental file). The roadmap follows the IC2 Alternatives Assessment Guide (2017) with additions from Northwest Green Chemistry's experience creating frameworks and conducting AAs, such as minimum ('showstopper') criteria defined for each module. The report includes ways to leverage modules completed by other entities, how to test for PFASs, and how to identify PFASs-free alternatives using state procurement policies. Strategic steps forward in a resource constrained and imperfect information environment will allow Oregon Department of Environmental Quality to make the most of the Roadmap.

NGC's priority selection criteria to scope an alternatives assessment based on the modules are:

- OR DEQ should employ best practices for **stakeholder engagement** to enable improved problem definition, information gathering, results, and adoption of results. Key stakeholders provide insight from their perspectives that may not be initially apparent to researchers. Key stakeholders include representatives from food packaging manufacturers, users, retailers, and innovators. Government agency staff, industry/trade groups, nonprofits, and politicians will also bring a unique set of concerns and knowledge to the issues.
- Based on NGC's work identifying AA best practices, we recommend a **decision analysis** method similar to the IC2 hybrid method. This method presents acceptable alternatives in a selection guide to promote informed decision-making based on stakeholder's varying application needs. Acceptable alternatives are those that meet minimum criteria for each module. Once these criteria are met, then the options should be subject to user preferences and needs.
- **Hazard** module recommendations include information on how to scope a chemical inventory, using a tiered approach to chemical hazard assessment, and with special considerations for polymers. The hazard module also includes showstopper criteria and guidance for identifying safer alternatives.
- NGC recommends setting a limit on **exposure** based on the hazards of the chemicals in question to eliminate unacceptable alternatives. A comparative exposure approach should be used to address exposure to workers, customers, and environmental receptors.
- **Cost and availability** module recommendations include comparing the retail price of PFASs-containing products and the alternatives. Cost should not be used to eliminate alternatives as any product currently available on the market is at a reasonable price point for at least some users. Cost should be considered across the life cycle to include costs from waste management. Economic analysis across the life cycle would present the full picture of hidden costs, e.g. cleanup and health impacts of PFASs, though it is likely cost prohibitive for the initial AA.
- We recommend using stakeholder input to define **performance** criteria for different uses that include minimum requirements and performance tests. Diverse users should be engaged, including from restaurants, cafeterias, caterers, hospitals, schools, prisons, and consumers, etc.
- The goal of the **social impact** module is to ensure that the product(s) preferred by the alternatives assessment do not shift the burden from one community of people to another unduly. Organizations that should be involved in the social impact module in Oregon are OPAL Pdx, Beyond Toxics, and the Environmental Justice Task Force, among others
- To address the **materials management** module, a holistic consideration of the product from feedstock to end of life should be conducted. This includes impacts from feedstocks used and

wastes generated and managed, as well as a consideration of how the product may fit into the circular economy.

- The overall goal of the **life cycle** module is to take a comprehensive view of product impacts across the life cycle, to identify opportunities for innovation and improvement, and to avoid burden-shifting. This module builds on results from previous modules and considers how the product fits within the broader system. Life cycle thinking helps to identify hot spots and opportunities for innovation. Life cycle assessment is important for verifying assumptions.

This report does not include gathering data and reporting the results of an alternatives assessment. However, the researchers have compiled information on alternatives gathered by NGC and building on the work of other groups. A variety of alternatives exist for each packaging technology type and are laid out by material types, molded fiber technologies and coatings and other treatments. The report includes a technology map, a table of alternatives representing each technology a supplemental Excel file with extensive detail on the product, its manufacturer, and PFASs screening test results if available.

Some Recommended Next Steps:

An AA report is a snapshot in time and should be accompanied by an implementation plan. The plan should include strategies and resources for ongoing identification and evaluation of emerging alternatives, for driving and measuring adoption of alternatives, and for integrating other important information. Novel information may emerge over time including new toxicology studies, changes in economics, and new waste management methods. Oregon should consider collaborating with other governmental agencies and key stakeholders to create an implementation plan for the proposed AA. Additional recommendations for next steps include:

- Publicly state Oregon’s priorities for PFASs free products. For example, as with a waste hierarchy, and consistent with OR’s materials management vision, OR DEQ could state that its priorities are 1) to avoid products with hazardous chemicals to which people and the environment will be exposed across the product life cycle and 2) to promote a circular economy that eliminates waste at the source and recovers materials at the highest possible value for reuse. This will clarify how existing statements on sustainability apply to food packaging.
- Develop promotional and educational materials for diverse users explaining the issue and describing how to select PFASs-free alternatives.
- Identify additional classes of chemicals to eliminate. For example, ortho-phthalates have been identified by the Food Packaging Forum as a priority for replacement in food packaging.
- Create or revise procurement policies to purchase PFASs-free food packaging. Appendices A, B and C in this report provide detailed information, including pros and cons, of test methods, standards and certifications. Some certifications exclude PFASs and others do not. The European standards based on EN13432, generally exclude PFASs due to a 100 ppm fluorine limit, while US standards do not. However, some US standards (i.e. BPI certified compostable) are being updated to address this issue.
- Identify products as PFASs-free by:
    - Testing and making a list of PFASs-free options available in Oregon.
    - Using the CEH list as a starting point, but keep it updated, as products change over time.
    - Using compostability/biodegradability certifications such as TÜV AUSTRIA Seedling Logo or post-2019 BPI compostable that also include limits for fluorine.
    - Consider supporting or developing a certification for simply PFASs-free products, as the compostability/biodegradability portion of these certifications is not relevant to Oregon currently due to Oregon composters declining compostable food packaging.

Introduction

The Oregon Department of Environment (OR DEQ) initiated the Roadmap for Evaluating Alternatives to Food Packaging Containing Per- or Polyfluorinated Substances (PFASs) to gain insights that will inform applied research and agency policies. OR DEQ strives to eliminate waste and toxics via its policies and to avoid adoption of regrettable alternatives. Preferred alternatives are those consistent with agency objectives, are based on information derived from credible science, and optimize the well-being of Oregon residents, the environment, and stakeholders throughout the value chain. Inclusion of workers and businesses involved, from resource extraction through manufacturing and end of life, ensures that this AA is practical and avoids burden shifting. Several other states have taken, or are in the process of taking, action to drive procurement of food packaging materials that are free of PFASs including Washington, Minnesota, and New York.

In this report, we synthesize previous work by Northwest Green Chemistry (NGC) and others identifying currently-used food packaging products that have been found to contain PFASs and available alternatives that are PFASs-free and potentially safer alternatives. Food packaging products containing PFASs are primarily plant-fiber-based, single use products including but not limited to wraps, liners, take-out clamshell containers, bags, bowls/soup containers, trays, and pizza boxes. Available alternatives provide the same services as the PFASs containing products but are free of all PFASs. The alternative products may be derived from completely different types of materials such as plastic, metal, or clays, or they may be plant-fiber based but treated mechanically or with non PFAS additives to meet performance requirements. The feasibility of different use scenarios should be considered, such as transitioning from disposable single-use products to multi-use products.

Alternatives assessment (AA) is an applied research process that supports the substitution of chemicals of concern in products or processes with inherently safer alternatives, thereby protecting and enhancing human health and the environment (IC2, 2017). At its best, it provides a balanced and comprehensive approach to considering the impacts and tradeoffs associated with various existing and emerging options to help users make informed decisions and to drive the adoption of safer alternatives. It can also inform product design and drive innovation. AA can be done at different levels of comprehensiveness. The more comprehensive the assessment, the more data and resource intensive it becomes. However, the use of AA does not guarantee success in substituting safer alternatives. First, safer alternatives must be available; second, those alternatives must be acceptable with respect to cost, performance, and social perspectives; and third, there must be drivers to move the market toward adoption of the alternatives.

Sustainable materials cannot be reduced to a single attribute. For example, a product that is bio-based may have lower environmental impacts, but it is still not a sustainable material if it contains toxic chemicals and generates problematic wastes. Sustainable materials approximate the ideal laid out in the principles of Green Chemistry and Green Engineering and in the Materials Management in Oregon 2050 Vision and Framework for Action (OR DEQ, 2012). Identifying sustainable materials using AA should be based on the Commons Principles for Alternatives Assessment (2012, p.1):

- REDUCE HAZARD: Reduce hazard by replacing a chemical of concern with a less hazardous alternative. This approach provides an effective means to reduce risk associated with a product or process if the potential for exposure remains the same or lower. Consider reformulation to avoid use of the chemical of concern altogether.

- MINIMIZE EXPOSURE: Assess use patterns and exposure pathways to limit exposure to alternatives that may also present risks.

- USE BEST AVAILABLE INFORMATION: Obtain access to and use information that assists in distinguishing between possible choices. Before selecting preferred options, characterize the product and process sufficiently to avoid choosing alternatives that may result in unintended adverse consequences.

- REQUIRE DISCLOSURE AND TRANSPARENCY: Require disclosure across the supply chain regarding key chemical and technical information. Engage stakeholders throughout the assessment process to promote transparency in regard to alternatives assessment methodologies employed, data used to characterize alternatives, assumptions made, and decision-making rules applied.

- RESOLVE TRADE-OFFS: Use information about the product's life cycle to better understand potential benefits, impacts, and mitigation options associated with different alternatives. When substitution options do not provide a clearly preferable solution, consider organizational goals and values to determine appropriate weighting of decision criteria and identify acceptable trade-offs.

- TAKE ACTION: Take action to eliminate or substitute potentially hazardous chemicals. Choose safer alternatives that are commercially available, technically and economically feasible, and satisfy the performance requirements of the process/product. Collaborate with supply chain partners to drive innovation in the development and adoption of safer substitutes. Review new information to ensure that the option selected remains a safer choice.

This report is not an alternatives assessment. Rather, it is a roadmap for using AA based primarily on the Interstate Chemicals Clearinghouse Alternatives Assessment Guide. This report does the initial work of scoping the AA and identifying alternatives. It also recommends which attributes to consider based on the modules in IC2 AA Guide. It helps prioritize information needs, including information on key test methods. Finally, it recommends an approach for decision analysis that results in identifying functional and cost-effective products that are inherently safer but that also mitigate waste, life cycle, and negative social impacts. As a roadmap, it is designed to help OR DEQ integrate information being generated by other organizations and jurisdictions working to eliminate PFASs containing food packaging and to prioritize information needs to meet OR priorities. This AA roadmap also provides a test case for applying AA in support of Oregon's Sustainable materials framework (OR DEQ, 2012).

The Alternatives Assessment Roadmap

The Interstate Chemicals Clearinghouse (IC2, 2017), in its Alternatives Assessment Guide, states that "The objective of an alternatives assessment is to replace chemicals of concern in products or processes with inherently safer alternatives, thereby protecting and enhancing human health and the environment" (p. 3). Alternatives assessment (AA) is a new and evolving field at the nexus of science and policy. Northwest Green Chemistry (NGC) recently completed one of the first AAs using the IC2 AA Guide (2017) to identify alternatives to copper-based recreational boat paints, which are slated for phase-out in the recreational boat market in Washington. The AA included assessment of available alternatives using the lens of hazard, exposure, cost, availability, and performance. Alternatives ranged from coatings with alternative biocides, to biocide-free coatings to non-coating technologies. Based on this work, NGC identified promising practices for AA and identified key needs for further work in the field.

The process of an AA can be broken down into six steps (Figure 1), including 1) identifying chemical(s) of concern 2) conducting an initial evaluation or exploratory research of the subject being investigated 3) defining the scope of the AA 4) identifying alternatives to the chemical(s) of concern, 5) assessing the alternatives and determine any viable options that do not lead to regrettable substitutions, and 6) taking action on the results. The IC2 Guide describes steps 1-5; step 6 has been identified by NGC as necessary for the AA to impact human and environmental health. This roadmap fulfills steps 1-4 and defines the data needs and criteria for step 5, but it stops short of data collection for the assessment process. It is important to note that steps 3 and 4 require additional stakeholder input.

ALTERNATIVES ASSESSMENT STEPS TO ELIMINATE PFASs FROM FOOD PACKAGING

Step 1: Identifying Chemical of Concern

OR DEQ specified PFASs as chemicals of concern in food packaging.

Step 2: Initial Evaluation

Consider removing PFASs with no other changes. Will products with PFASs function if PFASs are eliminated?

Step 3: Project Scoping for Alternatives Assessment

Engage key stakeholders, select assessment modules & decision framework. NGC recommends all modules & using a hybrid selection guide.

Step 4: Identify Alternatives

Including non-fluorinated alternatives; reusable products; & coatings, films, & barriers

Step 5: Assess Alternatives

Alternatives are assessed using collaborative efforts between NGC & OR DEQ's Materials Management. **Repeat any necessary steps.**

Step 6: Take Action

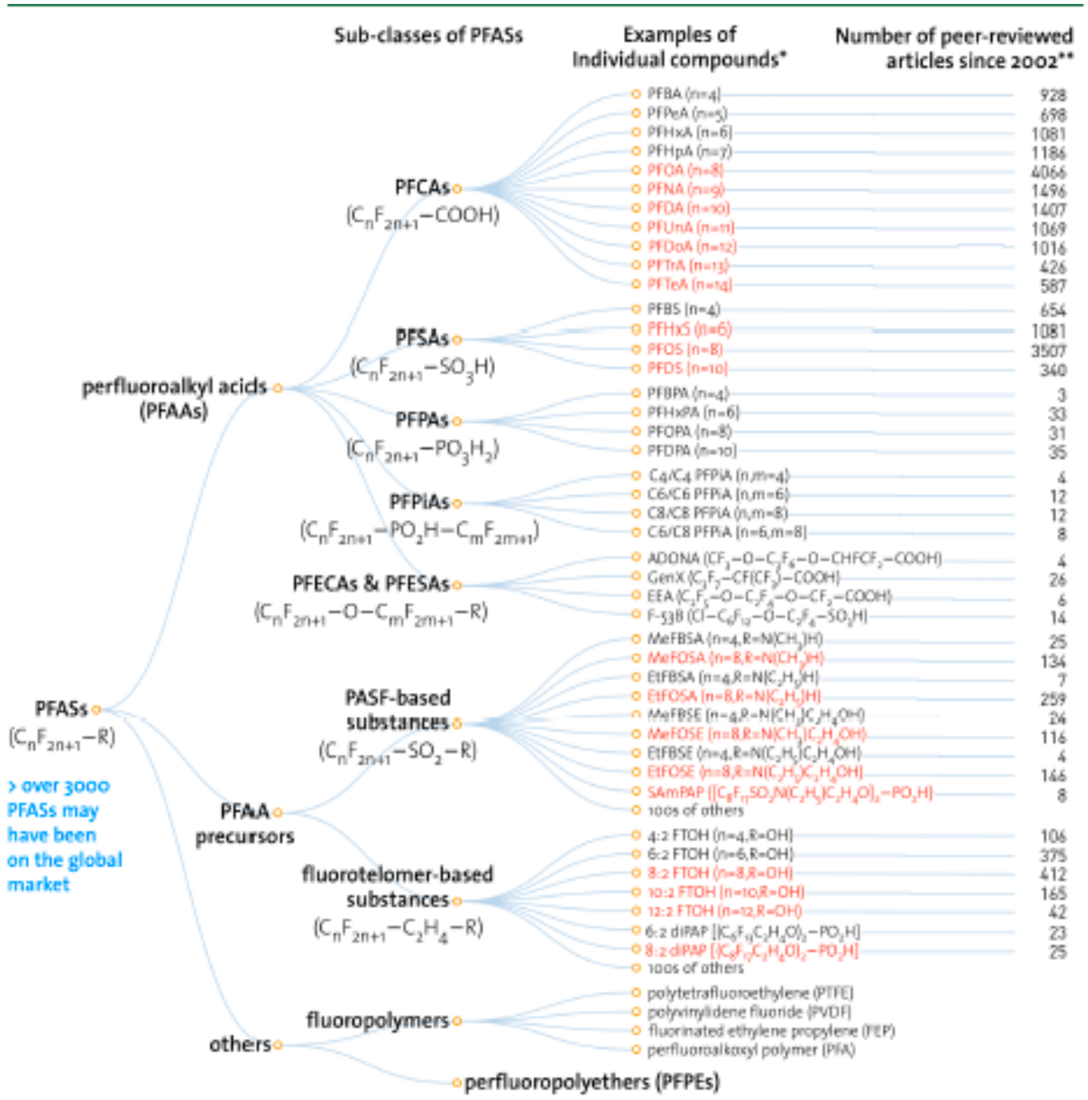
Create or revise policies; collaborate; implement changes; drive adoption; evaluate; update AA

Figure 1. The six steps of the OR DEQ Roadmap for Alternatives Assessment (AA).

Step 1. Identifying the Chemical of Concern

Goal: Specify the chemical(s) of concern that are the focus of the AA, reason(s) for concern (e.g. hazard, risk, waste/litter, emissions), and their usage.

Though identifying the chemical of concern is listed as the first step, it is common that the chemicals of concern (CoCs) have already been identified outside of the AA process. For this work, OR DEQ identified PFASs as a chemical class of concern in food packaging.



* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Figure 1. "Family tree" of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAs and their major precursors).

Figure 2. PFAS class and subclasses with examples of individual compounds within each subclass (Wang et al., 2017, p. 2510).

Buck (2011) defines PFASs as a chemical class, with several subclasses, characterized by the strong carbon-fluorine bond. PFASs are organic chemicals containing at least one fully fluorinated carbon atom (Scientific Guidance Panel Biomonitoring California, 2018). Estimates of the number of PFASs currently in products or the environment from previous manufacturing range from 3000-5000 (Buck, 2011; DeWitt, 2015; OECD 2018). Based on concerns about harm to human and environmental health, major U.S. chemical manufacturers ceased production of high profile PFASs, PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid), though production continues outside the U.S. (Lau, 2015). In this report, the term PFAS is used to apply to all chemicals in the class including precursors, metabolites and environmental degradation products that may degrade to form PFASs of concern (DeWitt, 2015). Figure 2 shows the class and subclass categorization completed by Wang, DeWitt, Higgins, and Cousins (2017) and indicates which substances have been subject to regulatory or voluntary phase-out action.

PFASs in Single-use Food Packaging

Fluorinated chemicals have been used for the past several decades as non-stick, grease, oil, and water-resistant coatings on a variety of products including food packaging. Fluorinated chemicals provide advanced chemical and physical properties, particularly related to heat, water and grease resistance, while being highly stable compounds. High heat resistance makes them function as fire suppression fluids. Their slick surface has warranted use for non-stick surface applications. Because they resist both water and oil, they have been used for clothing, equipment, carpets and much more to provide moisture and stain resistance. For single-use food packaging, heat and fluid (oil and water) resistance is a useful property that allows a variety of hot and cold foods to be contained for short durations without having the container fail, enabling consumers to store their un-eaten foods for later consumption.

Multiple methods for applying PFASs to food packaging materials exist (Trier 2018). The base material for most food packaging that contains PFASs is molded fiber. In these applications, PFASs are typically mixed in to the bulk material as an additive, rather than as a coating, which is more common for paper and paperboard. This process requires less steps and equipment than alternatives, decreasing costs and time. For post-production application, paper can be exposed to a solution of PFASs prior to pressing through rolls or against a hot steel drum, followed by drying (Trier 2018).

PFASs in food packaging are not necessarily bound tightly to the matrix. Researchers found that PFAS additives in food packaging paper migrate into food during package use (Begley, Hsu, Noonan, & Diachenko, 2007; De Witt, 2015; US FDA, 2007). Users can be exposed if the PFASs leach out of the food packaging into the food, and these chemicals can leach into the environment when the food packaging is composted, littered, or otherwise disposed of. While the rest of the packaging may break down, the PFASs will not in standard environmental conditions, or even the optimized conditions in an industrial composter. Migration of PFASs into food or other media is dependent on the amount, type, and chain length of the PFASs used, the contact time, the type of food or other media (e.g. predominantly fat - or water-based), and the temperature. Notably, even brief contact times can result in significant migration if the temperature is high and the media contains emulsified fats. In general, shorter-chain PFASs have been found to have higher migration efficiencies than long-chain analogues (Schaider et al., 2017). A comparison of PFASs exposure via other sources (air, water, dust, treated carpeting, and apparel) suggested that diet is an important source of these compounds (Tittlemier et al., 2007).

The problem of PFASs in food packaging is associated with compostable food service ware. Oregon does not currently compost food service ware and its composters have taken a strong stance against ever composting non-food products like these (Oregon Composters, 2019). The composters claim nine points on why composting food service ware may be detrimental, either to the environment or to their business model:

1. Products do not always compost, as expected.
2. Contamination happens.
3. Products hurt resale quality.
4. Composters cannot sell to organic farmers if products included.
5. Products may threaten human and environmental health.
6. Products increase costs and makes composters' jobs harder.
7. Just because something is compostable does not make it better for the environment.
8. In some cases, the benefits of recycling surpass those of composting.
9. Good intentions are not being realized.

Some of these points do not include a full consideration of the system, ignoring potential benefits of the diversion to compost of additional food from food service ware or lack of infrastructure for cleaning and recycling food service ware. Other points are currently being addressed by compostability certifiers, the push for product ingredient transparency, and by the proposed alternatives assessment work here. Until these issues are addressed, it is unlikely that Oregon's composters will change their stance. Regardless of their lack of acceptance by Oregon composters, compostable food service ware products are still used in Oregon. The use of these products results in exposure to workers and consumers. Disposal of these products in landfills results in PFASs exposing humans and the environment by:

- leaching to the subsurface and contaminating groundwater (Hamid, 2018).
- volatizing into air and contributing to elevated PFASs concentrations in the air near landfills (Hamid, 2018).
- leaching and subsequent treatment in a wastewater treatment plant, where they are not effectively removed and are released with treated wastewater and as part of biosolids (Hamid, 2018), which may be applied to agricultural land and taken up by plants (Lee, 2014).

Quantities emitted are small compared to a firefighting training ground, measured at ug/g space in soil at a firefighting training group (Baduel, 2015) versus ng/L to ug/L in landfill leachate (Hamid, 2018) or ng/g measurements for a specific PFAS sub-class in biosolid amended soil (Lee, 2014). These measurements are hampered by detection methods, which look at specific species or classes without taking a holistic view of all PFASs present (Hamid, 2018). However, even the emission of small quantities poses a risk when the substance is persistent and bio accumulative; 100 ng/g to 58 ug/g measurements were found bioaccumulated in plants grown in soil in the 0.1 – 138 ng/g range (Lee, 2014). Without considering the alternatives via an alternatives assessment, regrettable substitutions may occur. Further, no clear solution to the waste generated from food service ware exists in Oregon, and an alternatives assessment may be an avenue for identifying preferable materials and products with beneficial end of life programs.

Scope of Packaging for the Alternatives Assessment Roadmap

Fluorinated chemicals are found in a small subset of single-use food packaging products. Any molded fiber single-use food container without a plastic liner is likely to have fluorinated chemicals present. Researchers tested approximately four hundred fast food packages across the United States and found more than half of the dessert and bread wrappers contained PFASs (Schaider, et al., 2017); see Figure 3.

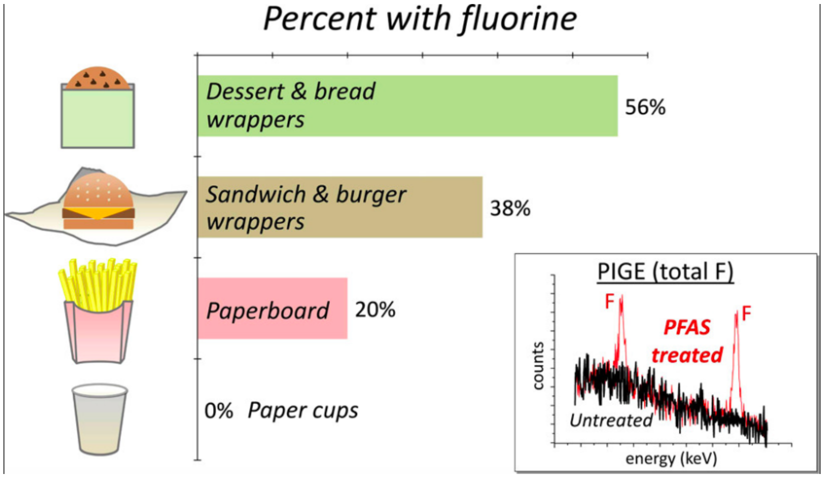


Figure 3. Percent of food packaging with fluorine from nationwide study (Schaider et al., 2017 p. 105).

A recent request for proposals for alternatives assessment work put out by the Washington Department of Ecology included the following (non-exhaustive) list of food packaging products where PFASs are likely to be used (Table 1).

Table 1. Examples of food packaging where PFASs may be used.

MARKET SEGMENT	PACKAGE TYPE	BASE MATERIAL
Quick Service Restaurants (QSR): such as national brands or local chains	Wraps/Liners	Paper
	Pinch Bottom Bags	Paper
	Flat Bottom Bags	Paper
	Clam Shells	Corrugated

MARKET SEGMENT	PACKAGE TYPE	BASE MATERIAL
		Board
		Molded Fiber
	Cartons	Board
		Molded Fiber
	Bowls/Soup Containers	Board
	Pizza Boxes	Corrugated
Food Service (FS): such as private restaurants, hospitals, institutions, or groceries	Trays	Board
		Molded Fiber
		Corrugated
	Cartons	Board
	Take Out Packages	Board
		Molded Fiber
		Corrugated
	Pizza Boxes	Corrugated
	Boxes	Board
		Corrugated
	Bowls/Soup Containers	Board
	Bakery Packaging (bags/liners)	Paper
	Deli Packaging (wraps/liners/interleaves)	Paper
	Bread Bags	Paper
	Prepared/Ready-to-eat Food Containers	Board
Consumer Packaged Goods (CPG): such as items sold in retail stores	Confectionary/Candy Wrap	Paper
	Snack Bags	Paper

MARKET SEGMENT	PACKAGE TYPE	BASE MATERIAL
	Microwave Popcorn Bags	Paper
	Pet food bags	Paper

(WA DOE, 2018, p. 6)

In addition to its use in the product, PFASs may be used in the manufacturing process as a mold release agent (Wang, 2007). A recent screen of food packaging products found high fluorine levels in a bowl made from polylactic acid (PLA), which normally does not contain PFASs. The manufacturer traced this contamination to the fluorinated mold release agent used in its production (CEH, 2018).

Human Health and Environmental Impacts

In May of 2015 a group of approximately 200 scientists signed The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs) to address mounting concerns about fluorinated chemicals (Blum et al., 2015). The statement reports adverse human and environmental health effects found to date, while addressing the need for scientists, government bodies, industrial manufacturers, and consumers to take part in creating solutions to this problem. Within the last few decades, sufficient evidence has emerged to convince manufacturers and other decision makers that these chemicals are hazardous. In addition, PFASs and their transformation products are highly persistent and bio-accumulating, with longer chain PFASs having a higher bioaccumulation potential than shorter chain (DeWitt, 2015). PFASs that are transformed in the environment biodegrade into other PFAS species that are persistent. As a result, a voluntary ban of the chemical degradation product known as perfluorooctanoic acid (PFOA), typically found in highly fluorinated chemical products, went into effect as part of the US EPA's PFOA Stewardship Program (US EPA, 2017). This program required a 95% reduction in product content and facility emissions of PFOA, precursors to PFOA, and related higher homologues by 2010, and a commitment to eliminate these chemicals from products and emissions by 2015. PFASs range in chain length with most academic literature published on the toxicity, persistence, and bioaccumulation associated with the C8 (8 carbon-fluorine bonds) chemicals. The impacts of C6 fluorinated chemicals (6 carbon-fluorine bonds) that have emerged as the alternatives chosen by some in industry to replace C8 fluorinated chemicals have been less studied. However, there is a growing body of research that indicates that short and long chain PFASs pose similar environmental and public health hazards (CEH, 2018; DeWitt, 2015).

Bioaccumulation and Routes of Exposure

Haukås, Berger, Hop, Gulliksen, and Gabrielsen (2007) reported that "multivariate analyses showed that the degree of trophic transfer of PFASs is similar to that of PCBs, DDT and PBDEs, despite their accumulation through different pathways" (p. 360). As a proteinophilic substance, PFASs do not bind to lipids like other chemicals of concern but are still passed up the food chain by binding to proteins (Xia, Dai, Rabearisoa, Zhao, & Jiang, 2015). Long-chain PFASs compounds bioaccumulate to the top of the food chain, as do the shorter-chain compounds, but to a lesser degree. However, there is one significant difference between the routes of exposure for the longer-chain compounds and the shorter-chain compounds; longer-chain compounds are less mobile compared to shorter-chain compounds. The primary route of exposure for both compounds for humans is through ingestion. Shorter-chain compounds can travel and enter through contaminated drinking water and are harder to remove (Lau, 2015). Longer -chain PFASs have a lower tendency to bioaccumulate through drinking water but a higher tendency to accumulate through other direct oral routes of exposure (CEH, 2018).

Breakdown products of fluorinated compounds, such as the short chain breakdown product perfluorohexanoic acid (PFHxA) has a half-life of 32 days, whereas the long chain breakdown product PFOA has a half-life of 3.8 years in a human system (Lau, 2015). The biological half-life of a chemical is the time required for the amount of that substance in that biological system to be reduced by half (PAC, 1994). Other studies involving both animal and human testing have shown that shorter chain PFASs have lower bioaccumulation potential than long chain PFASs, as well as shorter half-lives in human blood (Allen, 2016). While this constitutes a reduction in bio-persistence, it does not make the chemical a good choice for use in food contact materials.

Persistence

The perfluorylalkyl moiety of PFASs is highly resistant to degradation and transformation. Due to the high electronegativity of fluorine, carbon-fluorine bonds are both shorter and stronger than carbon-hydrogen and other carbon-halogen bonds and are considered the strongest bond in organic chemistry (O'Hagan, 2008). This further influences neighboring carbon-carbon bonds, such that the bond between carbons in the perfluoroalkyl chain is stronger than similar carbon-carbon bonds in a fully hydrogenated chain (Trier, Taxvig, Rosenmai, & Pedersen, 2017). Fluorine is a poor leaving group, and requires high ionization energy for extraction (Kissa, 2001). Together, these properties make the perfluoroalkyl moiety of PFASs resistant to chemicals, such as acids and bases, heat, and abrasion (Trier et al., 2017).

While the perfluorylalkyl moiety is stable, the functional groups on it may undergo transformations once in the environment. The net result is not the biodegradation of PFASs, but rather the interconversion of one PFAS species to another PFAS species with no net loss of PFASs. For example, fluorotelomer alcohols (FTOHs) are converted to corresponding perfluorylalkyl acids (PFAAs), which are extremely persistent (Trier et al., 2017). This lack of complete biodegradation contributes to its interest as a class of chemicals of concern.

Toxic Effects to Humans and the Environment

Commonly used PFASs have been dispersed globally through use and are detectable in water, soil, sediment, wildlife, and human blood samples (DeWitt, 2015). This means that any toxic effects that are present in these chemicals can be found in a range of environmental media. PFASs in blood are ubiquitous, found in almost all humans around the world, even in isolated areas in the Arctic, but in higher levels in urban areas (Lau, 2015). Exposed workers have up to 100 times the level of concentration of PFASs in their blood as the general population (Mundt, Mundt, Luippold, Schmidt, & Farr, 2007).

Toxic effects associated with PFOA and PFOS, found through epidemiological studies, include decreased average birth weight; kidney and testicular cancer; thyroid disease; decreased sperm quality; pregnancy-induced hypertension; and immunotoxicity in children (Bach, Bech, Brix, Nohr, Bonde, & Henriksen, 2015; Ballesteros, Costa, Iniguez, Fletcher, Ballester, & Lopez-Espinosa, 2017; Hekster, Laane, & de

Voogt, 2003). Other studies have reported that PFASs can cause human health effects such as increased cholesterol, increased uric acid, increased liver enzymes, lowered vaccine response, thyroid disease, osteoarthritis, diabetes, and ulcerative colitis (DeWitt, 2015). Toxicological studies in animals have linked these chemicals to "altered mammary gland development, reproductive and developmental toxicity, testicular cancer, obesity, and immune suppression" (Schaider, et al., 2017, p. 105). PFASs also cause animal toxicity that includes liver, immune system, developmental, endocrine, metabolic, and neurobehavioral toxicity (Hekster et al., 2003). These products were voluntarily phased out, but they can still be found in environmental media and are still being produced by global manufacturers outside the US.

Regulation

Since 2006, US EPA has reviewed 294 new PFASs and has regulated 191 through a combination of orders and Significant New Use Rules (SNURs). The US EPA is beginning the necessary steps to propose designating PFOA and PFOS as 'hazardous substances' through one of the available statutory mechanisms, possibly CERCLA Section 102 (US EPA, n.d.).

Washington State has enacted a multi-stage legislative effort that prohibits the manufacture and sale of food packaging with PFASs in any concentration starting in 2022. However, the State cannot enforce the law until the Washington State Department of Ecology (WA DOE) conducts and publishes an alternatives assessment that demonstrates safer choices are available. The AA will follow the guidelines of IC2 (2017) and include at least the chemical hazards, exposure, performance, and cost and availability modules. Alternatives must also be previously approved for food contact by the FDA (WA 2018 c 138 § 2).

Step 2. Initial Evaluation

Goal: Determine whether or not an AA is necessary. Can the chemical of concern be removed without replacement, and the product still functions?

Not all single-use food packing is likely to contain PFASs. Anything that is made with plastic or has a contact surface that is lined with plastic should not contain fluorinated chemicals. This is because the surfaces have inherent non-stick and grease, oil, and water resistance; or are not designed to contact food, thereby eliminating the need for these properties (CEH, 2018). Generally, the types of single-use food packaging that do not contain fluorinated chemicals of any kind are (CEH, 2018; Schaider, 2017):

- Coffee Sleeves
- Cold and Hot Beverage Cups and Lids
- Napkins
- Plastic (PLA) and Non-Molded Fiber Bowls and Plates; including Paper Soup Containers
- Plastic and Non-Molded Fiber Take-Out Containers
- Wooden Stirrers
- Cutlery

Testing to Ensure Products are PFASs-free

Recent reports exposing PFASs in food service ware used product testing to identify which products may contain intentionally added PFASs by screening for fluorine. For example, the Center for Environmental Health (CEH, 2018) conducted a study that identified food packaging with fluorine content using a technique known as PIGE (see Appendix A for detailed descriptions of test methods). Products with no or low fluorine were considered free of intentionally added PFASs, while products with high fluorine were suspected of containing intentionally added PFASs.

Products without fluorine were considered PFASs-free. Products with low fluorine were considered free of intentionally added PFASs; levels of PFASs in these products are sufficiently low that it would not provide water or grease proof properties to the final product. One possible explanation for the fluorine in these low fluorine products is contamination. The final category, high fluorine, was consistently ten times higher than the low fluorine category. These products were presumed to contain intentionally added PFASs for water/grease resistance, which was confirmed in a subset using standard liquid chromatography with tandem mass spectrography (LC-MS/MS) methods. The 2018 CEH study results appear in the accompanying Excel spreadsheet attached to the report and delimit the no, low, moderate, and high PFAS results of testing.

General Considerations for Testing

Test methods can be divided into two groups: Those that detect and quantify specific PFASs, and those that detect and quantify fluorine content. In general, methods that detect and quantify specific PFASs rely on mass spectrometry, typically tandem mass spectrometry, and the use of standards. The advantage of these methods is that each individual specific PFAS is identified and quantified, typically with a low limit of detection/quantification (LOD/Q). A survey of PFASs methods in 2013 found that the best LOD for waters was 0.4-5.2 pg/L, though LOQs of 0.28-0.58 ng/L were more common (Trojanowicz & Koc, 2013). The disadvantage of these methods is the time and resources required to run samples, the lack of detection of PFASs that aren't explicitly searched for, and the inability to quantify PFASs for which there is no available standard.

On the other hand, methods that detect and quantify fluorine content do not distinguish between different PFAS species, nor do they distinguish between organic fluorine in PFASs and organic fluorine in other molecules or inorganic fluorine. The advantage of these methods is typically the low cost and rapid testing time. The disadvantage is that lack of specificity of which molecules are present, and potential misattribution of fluorine to PFASs when other fluorinated organic compounds are present. When considering food service ware, PFASs are the expected fluorinated organic compound that would be present.

The preferred method for determining PFASs in diverse samples has been LC-MS/MS (Kempistry, Xing, & Racz, 2018; Valsecchi et al., 2013), and this is the only method for which standard methods have been developed by ASTM (ASTM D7979), US EPA (Method 537 for drinking water, unofficial modified Method 537 for other media), and ISO (ISO 25101) (ASTM, 2017; Shoemaker, 2018; US EPA, 2018; ISO, 2014). Unfortunately, it is limited by the number of PFAS species that can be identified and quantified in the same run.

Particle-Induced Gamma Ray Emission (PIGE) is a newer technique that measures total fluorine as a proxy for PFASs that does not require the destruction of the sample and is significantly less time and resource intensive (CEH, 2018). PIGE, with some samples confirmed by Combustion Ion Chromatography (CIC), was used by CEH in a recent scan of food packaging materials. Both of these methods simply measure total fluorine and require follow-up studies to confirm that the fluorine results from PFASs or knowledge that other sources of fluorine are not used with these products. Notably, the CEH (2018) only found one product out of 137 in which a high fluorine result came from PFASs from the manufacturing process as opposed to intentionally added PFASs. Similar techniques were successfully applied by Safer Chemicals Healthy Families and Toxic-Free Future (2018).

Despite the current lack of a standard method, we recommend using PIGE to scan for PFASs in food packaging materials. PIGE was confirmed as a valid rapid screening method for food packaging materials by Schaider et al. (2017). As needed with positive samples, PIGE could be followed with a standardized LC-MS/MS test to verify which PFASs are present, and to identify and quantify those PFASs. A non-targeted approach may be necessary if the PFASs used are not the ones currently covered by the standardized methods. PIGE is less resource and time intensive than other methods, and is suitable for food packaging, given the lack of false PFAS positives found by CEH (2018). All of the standard test methods use LC-MS/MS currently, though US EPA is working to develop additional standard tests, particularly for other sample types (US EPA 2018). ASTM D7968 is suitable for PFASs in food packaging, and the modified methods US EPA is currently working on are worth considering once they are developed. However, any of these follow-up methods require understanding which PFASs are present in order to select the correct method and standards; if common PFASs are present, this will not be a major barrier. PIGE would also be suitable for validating claims that food packaging materials are PFASs-free; a negative result would require no follow-up and would verify that the food packaging material is PFASs-free to the detection limit.

Standards and Certifications for Procurement

Rather than relying on testing by the Oregon, the state could require an independent certificate of analysis verifying that the product is fluorine-free or PFASs-free. In order to do so, the state would need to identify which testing methods and labs are suitable for this, and/or identify which certifications are suitable. In the recent CEH (2018) work, they observed that many products certified as compostable in industrial composting facilities tested high for fluorine. Standards and certifications that exclude PFASs include a 100 ppm limit on fluorine. These include:

- Standards
    - EN 13432
    - AS 4736
- Certifications
    - TÜV AUSTRIA, OK compost HOME/INDUSTRIAL, OK biodegradable SOIL/WATER/MARINE, Seedling Logo
    - DIN CERTCO, Seedling Logo, DIN-Geprüft test mark for industrial compostability
    - ABA, Seedling Logo, home compostable

  - BPI (starting Jan. 1, 2020)
  - Cedar Grove (starting Jan. 1, 2020)

For a detailed description of these standards and certifications, as well as common ones that do not exclude PFASs, see Appendices B and C. While these certifications can be used for procurement, their use would involve over-specifying, as compostability is not necessarily desired by Oregon. Setting a 100 ppm limit, verified by 3rd-party testing, would ensure that products are free of intentionally added PFASs. We would further recommend requiring a declaration that the final products are PFASs free and the manufacturing process is PFASs free to ensure other PFAS sources, such as mold release agents, are avoided. In order to avoid overburdening manufacturers, we recommend identifying materials and product types that do not contain PFASs that could be exempted from product testing. For example, PFASs are not used in the production of thermoformed plastics.

Existing Government Procurement Policies

Other states have enacted procurement policies for food packaging, including both the states of New York and Minnesota, which are compared in Table 2 (certifications) and 3 (procurement differences). This comparison may change in the coming months, as Minnesota's compostable food service ware contract specifications are in the process of being updated. While committee work has confirmed the desire to move to PFASs free ware in NY, updates to the policy are not yet available. Notably, these policies focus on compostable food service ware, which Oregon does not currently compost in industrial facilities.

Table 2. Certifications used for Minnesota and New York procurement.

MN Procurement	**NY Procurement**
AIB Vincotte Inter: OK Compost (Belgium) Australian Environmental Labeling Association Japan BioPlastics Association DIN CERTCO (European Union) Cedar Grove Commercially Accepted Items	ASTM 6400-04 – Standard Specification for Compostable Plastics ASTM 6868-03 – Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates
Biodegradable Products Institute (BPI)	

Table 3. Minnesota and New York procurement differences.

MN Procurement	NY Procurement
Procurement is for compostable food, beverage, and storage products	Procurement is for single use food containers (plates, bowls, hot & cold cups with lids, food trays & hinged containers)
When reusable food service containers are unavailable, compostable containers should be used, despite availability of infrastructure	When reusable food service containers are unavailable, compostable containers should be used (as long as there is a composting facility to accommodate)
Composting Specifications: None	Composting Specifications: All single use food containers (excluding hot and cold containers and lids) to the maximum extent be composted under ASTM 6400-04 for plastics and ASTM 6868-03 when coated, or if not applicable shall be biodegradable.
Composting Exception Specifications: None	Composting Exception Specifications: Hot and cold containers and lids shall meet one of the following: 1. Manufactured from bio-based material that is compostable or biodegradable 2. Manufactured from polymeric material (plastics/resins? With a minimum of 30% post-consumer recycled content (unless content is not allowed by USFDA) 3. Recyclable through a local or commercial program and labeled with a visually legible Resin Identification Code
Labeling Requirements: All compostable plastic products offered must bear a clearly visible, easily distinguished label or marking indicating the product's ability to be composted Text of the label or marking must include "COMPOSTABLE" Label and marking must be present on each individual item The State prefers the label or marking to be green in color and to include the logo of the certifying body	Labeling Requirements: If bio-based container is manufactured with polyethylene coated material, it is not compostable, and each container shall be marked to indicate it is not compostable, biodegradable, or recyclable.

MN Procurement	NY Procurement
Excluded Compounds: Per- and polyfluoroalkyl substances (PFASs) must not be added to products. To comply with this requirement, Contract Vendor must submit test results demonstrating that each proposed fiber-based product contains less than 100 ppm of fluorine. Information on testing protocol and recommended labs is available, upon request. If the revised price list does not contain fiber-based products, Contract Vendor does NOT need to submit test results. Only future proposed fiber-based products will need to be accompanied by test results.	Excluded Compounds: In accordance with Environmental Conservation Law section 37-0205, packaging shall not contain inks, dyes, pigments, adhesives, stabilizers, or any other additives to which any lead, cadmium, mercury or hexavalent chromium has been included as an element during manufacture or distribution in such a way that the sum of the concentrations levels of such lead, cadmium, mercury or hexavalent chromium exceed the following concentration level: 100 parts per million by weight (0.01%).
Other: None	Other: All packaging materials shall be made from reusable or recycled materials. All paper based packaging shall contain 30 percent post-consumer fiber by fiber weight. No foil or mylar packaging or excessive inner packing shall be used

Step 3. Scoping the AA

Stakeholder Engagement

Goal: Ensure stakeholders’ concerns are addressed, disseminate information to stakeholders, improve acceptance and adoption of results by stakeholders, improve criteria and metrics to ensure relevance to stakeholders.

The stakeholder engagement module in the IC2 (2017) AA framework allows for varying levels of involvement, ranging from a simple thought experiment by researchers to an open stakeholder engagement process. Stakeholder engagement enables improved problem definition, information gathering, results, and adoption of results. Key stakeholders provide insight from their perspective that may not be initially apparent to researchers (Nestler & Heine, 2018). However, stakeholder engagement can be time and resource intensive.

For this project, we recommend using the IC2 Guide (2017) Level 2 formal stakeholder process. It requires OR DEQ to seek identified stakeholder input in a structured process. The formal process allows the agency to ensure, “pertinent AA information is provided for stakeholder review and comment (and that) all comments are collected and responded to” (IC2, 2017, p.24). Stakeholders should be contacted as soon as possible in the AA process. It is particularly important early on to gather stakeholder input on which products should be included in the AA, and on gain consensus on the criteria for each module.

Stakeholders should include:

- Users: food trucks, restaurants, caterers, hospitals, schools, and prisons
- Waste management professionals: composters, recyclers, waste-to-energy, landfills, compost sellers, and users
- Manufacturers: of PFAS-containing food packaging products
- Manufacturers: of PFASs-free food packaging products
- Manufacturers and suppliers throughout the supply chain: of materials and coatings or other substances used in food packaging, e.g. paper manufacturers, converters, etc.
- Retailers
- Distributors of food packaging products
- Innovators: Researchers, entrepreneurs, and businesses creating disruptive innovations
- Local community members: Local politicians, community leaders, and environmental/social justice groups (see social impact section for more information)
- Representatives of the environment: Environmental non-profits
- Government representatives: Local, county, regional, and state representatives
- Industry/trade associations

All stakeholders invited should be asked to identify other relevant stakeholders, who should then be invited to join the process. Contact can primarily be on-line and over-the-phone using conference calls for large group discussions, but some in-person contact at relevant events (e.g. restaurant, food truck, or food packaging related conferences or events) can assist with reaching additional stakeholder perspectives (Nestler & Heine, 2019). Interviews should supplement large-group meetings, particularly focusing on stakeholders who have not spoken up during the large-group meetings.

To inspire and motivate stakeholders involved in collaboration, it is important to designate a champion according to best practices in stakeholder engagement (Bryson, 2018; Intersector Project, n.d.; McDermott, Moote, & Dank 2011). This champion can be an individual or an entity, and the role of this champion is to build buy-in, credibility, and support for working together (Auwarter, Holly, Mareld, & Montgomery, 2016). Champions should be able to work with people in a way that brings out others' creativity and desire for change and have a network of experts to call upon (Auwarter et al., 2016). Groups also need an internal facilitator considered to be trustworthy, approachable, and impartial by participants (Ansell & Gash, 2008; Reed, 2008). Trusted facilitation is especially important in situations in which conflict is likely, for example, between chemical companies and environmental advocates, or between competing companies (Reed, 2008).

Stakeholder engagement should be used to further define the scope of the AA while ensuring that the results will be practical and increase the likelihood of adoption of results. For example, stakeholders should be involved in identifying alternatives and determining which alternatives are assessed. Numerous alternatives exist, and stakeholders can assist in narrowing the scope to the most viable. If the alternatives stakeholders are most interested in are not considered, they may choose to use those regardless of the lack of information.

This module can be made less resource intensive by limiting 1:1 and in-person engagement. We do not recommend eliminating active stakeholder engagement or changing to level 1 in the IC2 Guide (2017), which is a thought experiment and does not involve actually speaking with stakeholders. Rather, contact can be limited to conference calls, workshops and webinars to minimize resource use. Focus groups for particular topics or groups of stakeholders can also provide insight quickly and replace larger stakeholder input sessions, where appropriate.

This module can be made more resource intensive by involving stakeholders more directly in the decision-making process, such as by forming committees or working groups that advise on every step of the process. Some subgroups or committees may be desired for certain special interests. For example, this project may warrant an in-depth discussion of compostability vs recycling and the challenges posed by consumer sorting, collection, professional sorting, composting/recycling, and the sale/usage of the resulting compost/recycled material.

Decision Analysis

Goal: Guide assessors through the analysis of large amounts of often conflicting data to select preferred alternatives and empower users to make informed decisions about chemical or whole-product substitution.

The IC2 Guide (2017) describes three options for decision analysis: sequential, simultaneous, and hybrid. In the sequential method, assessors assess modules one at a time, and based on the results, eliminate some products before proceeding to the next module. In the simultaneous method, assessors assess all modules at the same time, and use the results in concert using a multi-parameter analysis to eliminate products. In the hybrid method, certain modules are prioritized and completed first using the sequential method, followed by simultaneous assessment of remaining modules using a multiparameter analysis. For example, assessors may complete the hazard module and eliminate some alternatives before proceeding to assess performance, cost & availability, and exposure simultaneously.

We recommend the hybrid approach to decision analysis with a variation used by NGC as part of its work to evaluate alternatives to copper-based recreational boat anti-fouling coatings. This approach establishes ‘showstopper’ criteria in individual modules similar to the sequential approach. However, from there it diverges from the sequential approach in a useful way. Instead of making decisions for stakeholders and assuming all stakeholder needs are similar, the assessment results for each product are presented in a matrix or other user-friendly Selection Guide (SG) format that is designed to help diverse users make an informed decision about the product(s) they select. Products would need to be separated into those that are specific final products versus those that are alternative coatings or treatments that could be applied to a final product. The group conducting the AA does not evaluate the options that make it through the first pass/showstopper criteria. This hybrid approach allows for different users to apply their own values, performance needs, and preferences. All of the available options will have met minimum criteria to ensure that they are inherently safer and more sustainable than the alternatives they will substitute.

For example, some stakeholders will value reusables over single-use disposable products and will prefer products such as the GO Box where infrastructure exists. Others may prefer single-use disposables that are commercially compostable for use in closed events with composting capacity. Still others may prefer products that are bio-based or recyclable in order to reduce their carbon footprints; others may require that products with such claims are backed by life-cycle assessments confirming that they do actually represent a reduction in emissions. Others may be especially cost sensitive or may be constrained by product availability. This process is related to the approach used by Consumer Reports (2018). Consumer Reports evaluates products based on what it deems to be the most relevant and discriminating criteria. In AA, those criteria are defined by the modules in the IC2 AA Guide (2017). For example, while Consumer Reports may report durability, energy consumption and cost for refrigerators, it does not rank them by space capacity or whether or not the freezer is on the top or the bottom or whether it has two doors or one. The final decision about product fit is left to consumer preference and need.

Stakeholder input should be used to ensure that the Selection Guide covers all of the important and discriminating attributes needed to support decision making about this set of products, or if it would be more useful to develop Selection Guides for different product uses. For example, there could be Selection Guides specific to each product (e.g. soup bowls, clamshells, etc.) or specific to certain use parameters (e.g. acceptable for hot food vs cold-food only, or microwaveable, etc.). This hybrid decision approach method preserves the greatest choice for users while still eliminating unacceptable options.

Driving innovation with AA: For some functional uses, there may be no products that currently exist that meet the first pass requirements. The assessors should clearly identify these as innovation opportunities. Funding entities, such as government agencies or foundations may consider offering incentives, in the form of grants or loans, directed at these innovation opportunities. Other funding entities could consider setting up a competition similar to the X Prize to encourage innovation. Investors may decide to invest in emerging start-up companies that seek to take on the innovation challenge.

Step 4: Identifying Alternatives

Goal: Broadly identify the universe of alternatives to the chemical of concern, including direct chemical substitutes, whole-product substitutes, and potentially disruptive innovations that approach product function differently.

Based on NGCs prior AA experience, we recommend that the scope of possible alternatives considered should be broad and include both existing and emerging options. Inclusion of a broad range of alternatives increases the likelihood that alternatives are found. It also increases the likelihood that the alternatives will not only be PFASs free, but that they will provide benefits across the full product life cycle. If the scope is too narrow, then innovative alternative materials and even innovative business models that mitigate impacts from food packaging products may be missed. While AA may be used to identify opportunities for incremental improvement, it can also help define specific challenges for chemical, engineering, or business model innovation. In coordination with OR DEQ's Toxics and Materials Management teams this AA roadmap provides a test case for applying AA in support of Oregon's Sustainable Materials Management Vision and Framework (OR DEQ, 2012).

The down side of broader inclusion is that less information may be available on new or emerging options. For example, users of new product types may have less experience with their performance; their initial costs may be higher than those for incumbent products, not reflecting future costs when brought to scale, and they may not be readily available in all locations.

AA is a snapshot in time and additional options may be identified as more stakeholders are engaged and new products are developed. Therefore, we advocate for consideration of both existing and emerging options including:

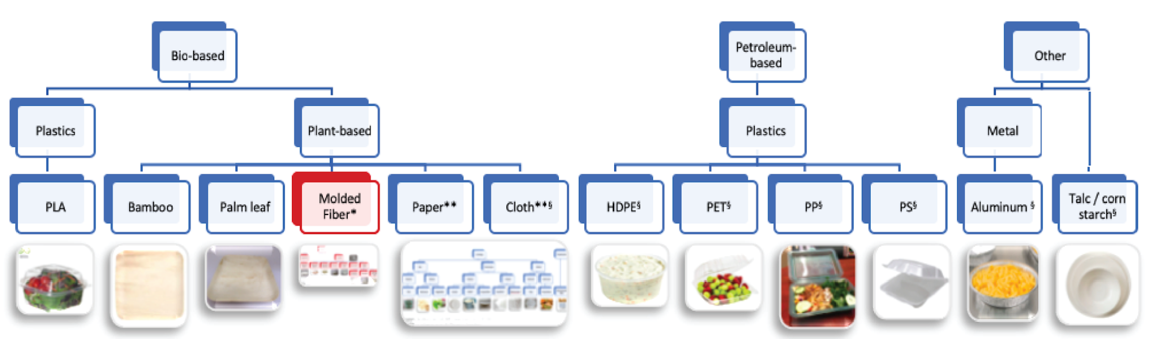
- Alternative bio-based materials, with or without coatings or additives to enhance performance (plant fiber, PLA)
- Alternative non bio-based materials that do not require PFAS additives to achieve performance specifications (e.g. aluminum, plastics, clays, etc.)
- Biodegradable, recyclable and reusable products

For example, Vibers (www.vibers.nl), a company based in the Netherlands, recently developing food service ware using locally grown elephant grass. If included and determined to be a preferable option, OR DEQ could use these results to encourage further development of this alternative in Oregon. Figure 4 provides a visual flowchart or map of available food packaging technology types. The supplemental file contains a compiled list of existing product, material and coating options from CEH (2018), CFE/CPA (2018), and NGC (2018) for this report.

Currently Identified PFASs-Free Food Packaging

There are numerous alternatives that may be sorted based on different attributes. A good first step is to consider the base material platform and the product functional uses. Not all materials will support all applications and it is useful to know the availability of alternatives for each functional use. Figure 4 (with parts a, b, and c) lays out a schema for comparing food packaging technologies broken out by 1) materials, 2) molded fiber feedstocks, and 3) coatings and treatments. The supplemental file links those categories to specific products. All technologies listed include examples that are suspected or known to be PFASs-free. This includes some examples of fiber-based products that claim to be PFASs-free. However, all molded fiber products tested by CEH contained PFASs. PFAS-free food packaging products may be sorted further based on material types, feedstocks, process treatments, and end of life management options.

Materials 4



Technologies with no notation include examples that have been tested as no F

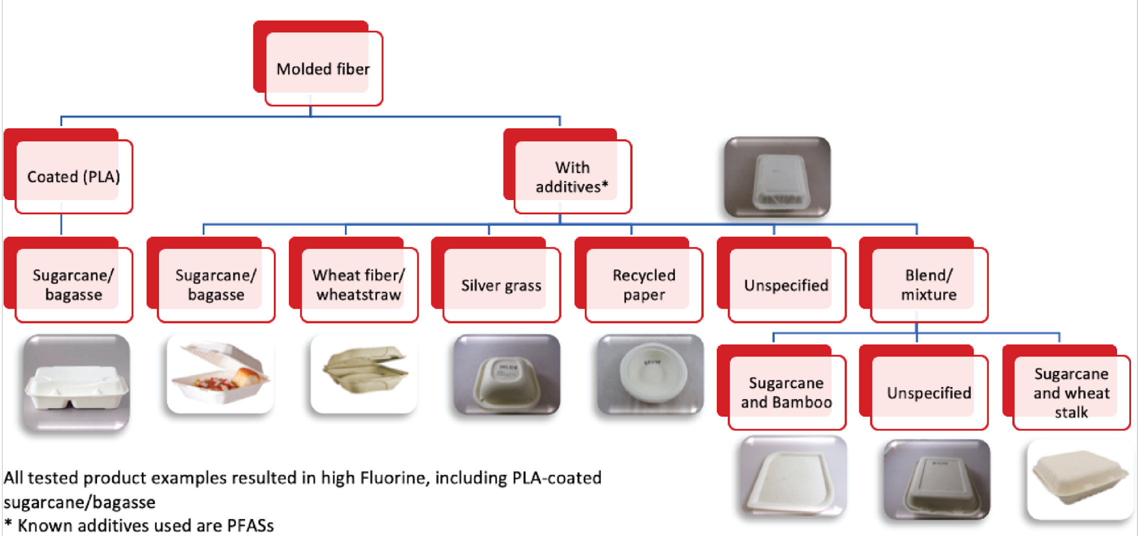
§ These products have not been tested, but are suspected PFAS-free

* Requires additives or coatings; all molded fiber tested by CEH was high for F

** Requires coatings or treatment; some are available without PFAS

Figure 4a. Technologies used for food service ware: Materials

Molded Fiber Feedstocks 4

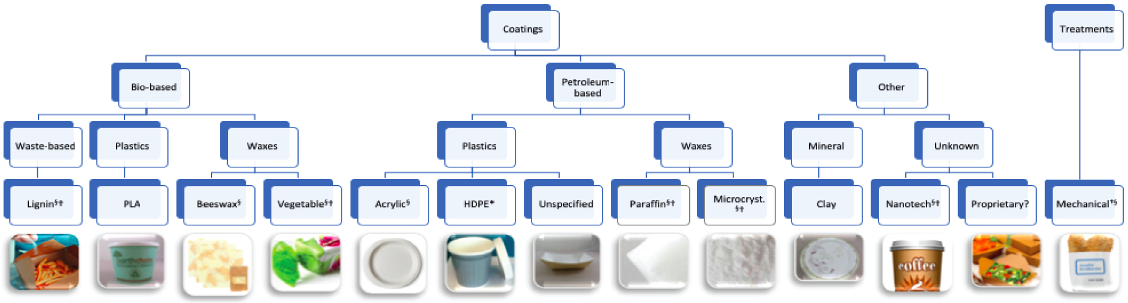


All tested product examples resulted in high Fluorine, including PLA-coated sugarcane/bagasse

* Known additives used are PFASs

Figure 4b. Technologies used for food service ware: Molded fiber feedstocks

Coatings & Treatments 4



Technologies with no notation include examples that have been tested as no F
§ These products have not been tested, but are suspected PFAS-free
* Example product tested as low F (CEH 2018)
† Available technology but product availability limited

Figure 4c. Technologies used for food service ware: Coatings and treatments

Step 5: Proposed Selection Criteria to Narrow the Scope of the AA

NGC recommends the use of modules for stakeholder engagement, materials management, life cycle, and social impacts, in addition to the four mandatory AA modules hazard, exposure, cost & availability, and performance. For each module, we created priority selection criteria to ensure that alternatives to products with highly fluorinated chemicals are not regrettable substitutions.

As discussed, we propose using a modified hybrid framework for decision-making. In this framework, an initial screening assessment is done with a defined set of modules using 'showstopper' criteria to eliminate unacceptable alternatives. For example, showstopper criteria in performance can set a minimum standard of acceptable performance. Further analysis of performance will distinguish between higher and lower performers. The showstopper step exists to rapidly eliminate unacceptable alternatives and save time and resources by not fully assessing eliminated alternatives.

Hazard

Goal: Ensure preferred alternatives are comprised of chemicals that are inherently less hazardous than the chemical/product of concern.

The hazard module allows for a comparison between the inherent chemical hazards of the chemical of concern (here, PFASs) and alternatives. *Reduce hazard* is the first principle in the Commons Principles for Alternatives Assessments (2012). It is also at the heart of the green chemistry and engineering – to *eliminate toxics in products and processes.* This module allows for the selection of inherently less hazardous options and guards against regrettable substitutions, a situation where the alternative is equally or more hazardous, than the original chemical or product of concern.

A recent report from Safer Made identifies numerous chemicals of concern currently used in food packaging (Mulvihill, 2019):

- 53 chemicals of concern intentionally added to plastic food packaging
- 20 chemicals of concern intentionally added to fiber food packaging, 12 of which are PFASs
- 12 chemicals of concern intentionally added to metal food packaging, 2 of which are PFASs
- 72 non-intentionally added chemicals of concern

The authors also noted greater transparency of the supply chain and greater disclosure of additives are essential for driving the adoption of safer alternatives. Without a robust assessment of the ingredients and hazards of alternatives to products containing PFASs, regrettable substitutions may occur.

This section covers:

- Building a chemical inventory
- Taking a tiered approach to chemical hazard assessment (CHA)
- Criteria to eliminate (showstopper) unacceptable alternatives, and to identify safer products

For this module, we recommend a tiered approach as opposed to following a specific level in the IC2 Guide.

Chemical Inventory

Goal: Identify chemicals relevant to each product across the product lifecycle.

A chemical inventory is a critical step in applying both the hazard and exposure modules and is used to determine which chemicals will be assessed. This involves defining the scope of the chemicals of interest, determining how chemicals will be identified, and setting clear thresholds for disclosure and assessment. Identifying all relevant chemicals will require cooperation from manufacturers and may require the use of non-disclosure agreements (NDAs) to protect confidential business information (CBI). Transparency and public disclosure should be preferred when possible.

The chemical inventory should be completed for all products that are currently available as well as for emerging technologies of interest. At a minimum, the chemical inventory includes all substances that are likely to be retained in, or migrate from, the food packaging. This includes any monomer(s), oligomer(s) and any known additives and residuals (impurities), including catalysts and performance additives (anti-oxidants, colorants, plasticizers, UV stabilizers, flame retardants, compatibilizers, etc.). Ideally, the inventory should provide insight into occupational hazards as well. Knowing the residuals provides information on the chemicals used in manufacturing. A more complete assessment requires inventorying chemicals used and generated across the product life cycle in order to assess hazard, exposure, life cycle and disposal/recycling impacts. Assembling a complete chemical inventory for each life cycle stage can be challenging because formulations are often proprietary, and information for all life cycle stages may not be available, even to manufacturers throughout the supply chain.

We recommend inventorying all intentionally added chemicals as well as residuals present in the use phase of the product life cycle, and all intentionally added or used chemicals during the manufacturing stage. *Residuals* as defined by the USEPA Safer Choice Program (Safer Choice) are ‘trace amounts of chemicals that are incidental to manufacturing. Residuals are not part of the intended chemical product but are present because of factors such as the nature of the synthesis and engineering pathways used to produce the chemical. Residuals include: unintended by- products of chemical reactions that occur in product formulation and chemical synthesis, impurities in an ingredient that may arise from starting materials, incompletely reacted components, and degradation products’ (US EPA 2012).

Depending on the product, some residuals are more problematic than others. For example, due to the use of PFASs as mold release agents, PFASs may end up in a products due to manufacturing, even though they are not added to provide grease or water repellency. Such residuals are referred to as ‘residuals of concern’. *Residuals of concern* as defined by Safer Choice are ‘residuals that fails to meet the criteria in the General Standard for carcinogenicity, mutagenicity, reproductive toxicity and other human health effects, or fails to meet the criteria for persistence, bioaccumulation and toxicity, as defined by the Final PB&T Rule’ (US EPA 2012).

Most chemicals have multiple names and need to be identified clearly using conventions such as Chemical Abstract Services Registration Numbers (CASRN), International Union of Pure and Applied Chemistry numbers (IUPAC) and others (EINECs, INCI). In theory, these identifiers are unique. However, some identifiers apply to general classes or groups of chemicals and more nuanced identification may be needed, such as for different forms of a chemical or molecular weight ranges. Additional data such as molecular structure and physical form help to refine the compound's identity. The chemical inventory includes the precise chemical identity, the chemical function, and concentrations or amounts (exact or ranges). We recommend using CASRNs to identify and distinguish all chemicals as a baseline, but to include additional specifications when available. This information may be used to determine that certain hazards do not apply to the specific form used in the product.

Clear thresholds are needed to determine which chemicals to include in the inventory and which to assess. One strategy is to set a concentration threshold, or de minimus level, at, or above which, a chemical constituent will be evaluated. Selecting a threshold may depend in part on the chemical's hazard characteristics. For example, endocrine disrupting substances are hazardous at very low exposure levels and thus a low threshold is appropriate. Safety Data Sheets provide precedent for using different disclosure levels for chemicals with different hazard traits. Carcinogenic chemicals above 0.1% must be reported while non-carcinogenic hazardous chemicals are disclosed above 1% (US EPA 2018). Some certification programs (e.g. Cradle to Cradle) link certification levels to the weight percent of chemicals disclosed. Example disclosure thresholds and criteria include:

- Specific chemicals known **not** to be present in a product.

- All intentionally used or added chemicals at any concentration for limited life cycle stages (e.g. use phase only).
- All intentionally used or added chemicals at any concentration at all life cycle stages.
- All intentionally added chemicals plus residuals at or above a concentration threshold.
- All intentionally added chemicals plus residuals present at or above a concentration threshold, plus residuals of concern at any concentration.

We recommend identifying all chemicals intentionally used or added along with residuals above 0.01% and residuals of concern at any concentration for assessment. Some people use a tiered and iterative approach to inventorying chemicals, starting with higher disclosure thresholds, and working to gather additional information at lower thresholds as feasible and relevant. The overall goal of this module is a comparison of materials based on hazard, so chemicals shared between all products may not need to be assessed. We recommend following a tiered and iterative approach that considers the kinds of comparisons desired. For example, alternative substances that function as a direct replacement to PFASs, using the same base material as PFASs-containing food packaging (e.g. alternative is a coating used on molded fiber), need only those intentionally used or added chemicals that are *different* between the PFAS packaging and the alternative packaging to be assessed. Chemicals that are shared between the PFAS packaging and the alternative packaging do not discriminate between products. However, all chemicals will need to be assessed to compare products outside of this limited scenario. The chemical inventory can be made more or less resource intensive by limiting or expanding the scope as follows.

- Life cycle stages included
    - Minimum: Use phase
    - Preferred: Use and manufacturing
    - Ideal: Use, manufacturing, and disposal/EOL
- Inventory thresholds
    - Minimum: All intentionally added ingredients. Residuals at or above 0.1%.
    - Preferred: All intentionally added ingredients. Residuals present at or above 0.01%
    - Ideal: All intentionally added ingredients, residuals at or above 0.01%, and all residuals of concern at any concentration, as defined in the US EPA Safer Choice standard (US EPA 2012).
- Disclosure
    - Minimum: Obtain publicly available information only.
    - Preferred: Companies provide ingredient disclosure under an NDA.
    - Ideal: Companies publicly disclose, providing full transparency.

Unfortunately, obtaining the same level of disclosure for every product is challenging. A mixture of disclosure levels further complicates decision analysis, as a lack of disclosure is not evidence of low hazard. Identifying all intentionally added ingredients, without identifying residuals, can result in regrettable substitutions, particularly if the manufacturing phase is not considered. For example, PFASs used as mold release agents can contaminate the final product despite not being intentionally added.

We recommend encouraging companies to provide full disclosure by rewarding them for disclosure in the AA process. For example, insufficient disclosure may be used as a criterion to exclude products from advancing in the AA towards the decision analysis.

Polymers

Polymers require special consideration. The United States, the European Union and others have established criteria and methods to screen for polymers of low concern (European Commission 2015). Polymers are generally unreactive, and their large size prevents them from crossing biological membranes. Hazards associated with polymers are usually tied to non-polymeric substances within the polymeric matrix including unreacted monomers, partially reacted oligomers, additives, etc. It is important to know the molecular weight (MW) ranges of substances in a polymer including residual monomers and oligomers. Lower molecular weight substances are more likely to migrate from plastic and, if toxic, will result in exposure. Therefore, MW is a screening criterion for identifying polymers of low concern. Typical thresholds used are < 500, > 500 and < 1,000, > 1,000 and < 5,000, > 5,000 and < 10,000, > 10,000 Daltons (Da). These thresholds are for screening purposes and cut off ranges may be shifted if warranted. For instance, ranges may be different for fluoropolymers (< 1,500 Da) or for higher molecular weight substances if accompanied by permeation enhancing substances commonly found in food contact materials (Geueke, Groh, & Muncke, 2018). When the perfluorinated moiety is present on a side-chain, degradation products may include mobile PFASs that need to be considered separately from the higher MW polymer. For polymers, we recommend identifying the molecular weight ranges of substances in the polymer, as well as the monomer, catalyst(s), any additives and processing aids used, and degradation products, particularly cleavable fluorinated side-chains.

Cooperation from manufacturers is necessary to generate a complete product inventory. However, even manufacturers may find it challenging to identify all chemicals involved in the production of a given product. Perfect information is not possible and there is no one single right way to set disclosure requirements. By communicating to manufacturers that their participation will influence future purchasing decisions, stakeholders who purchase products can be invaluable partners in convincing manufacturers to participate fully.

Transparency is important because information about what is known, and not known, about the chemicals used in production and manufacturing will support informed decision-making. We recommend preferring companies that provide full disclosure. Public disclosure is preferred over NDA-sealed disclosure; and more complete disclosure (e.g. including residuals as well as intentionally added ingredients, to a lower threshold, or covering more life cycle stages) over less complete disclosure. This aligns with the Commons Principles for Alternatives Assessment (2012), which recommends requiring disclosure and transparency.

This module can be made more or less resource intensive by limiting or expanding the scope of chemicals inventoried.

- Life cycle stages included
    - Minimum: Use phase
    - Preferred: Use and manufacturing
    - Ideal: Use, manufacturing, and disposal/EOL
- Inventory thresholds
    - Minimum: All intentionally added ingredients including monomers, MW range of oligomers, and catalysts. Residuals at or above 0.1%.
    - Preferred: All intentionally added ingredients including monomers, MW range of oligomers, and catalysts. Residuals present at or above 0.01% in final product.
    - Ideal: All intentionally added ingredients including monomers, MW range of oligomers, and catalysts, residuals at or above 0.01%, and all residuals of concern at any concentration, as defined in the US EPA Safer Choice standard (US EPA 2012). Clear identification of processing aids and other chemicals used in manufacturing.
- Disclosure
    - Minimum: Obtain publicly available information only.
    - Preferred: Companies provide ingredient disclosure under an NDA.
    - Ideal: Companies publicly disclose, providing full transparency.

Tiered Approach to Chemical Hazard Assessment

Goal: Efficiently and effectively assess hazard of chemicals on the inventory.

We recommend a tiered approach that begins by screening all chemicals using rapid and inexpensive chemical hazard assessment (CHA) methods, followed by progressively more resource intensive methods, as necessary. In this approach, the easiest sources are utilized first to eliminate products using “showstopper” criteria, and more detailed, resource-intensive assessments are used to further eliminate products using “showstopper” criteria and to distinguish between lower-hazard products. This process identifies products with acceptable hazard profiles while reducing costs.

Tiered assessment method:

1. Search for existing comprehensive chemical hazard assessments (CHAs). See the IC2 AA Guide for more detail on the different CHA methodologies (IC2 2017)
    a. Search for:
        i. Full chemical hazard assessments using the GreenScreen for Safer Chemicals (GS) methodology (Clean Production Action 2018) or the Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation (US EPA 2011)
        ii. Partial GS assessments or assessments done using the WA DOE Quick Chemical Assessment Tool (QCAT) method (WA DOE, 2016)
    b. Search at:
        i. IC2 CHAD: http://www.theic2.org/hazard-assessment
        ii. GS Store: https://www.greenscreenchemicals.org/gs-assessments
        iii. Data commons: https://commons.healthymaterials.net/

        iv. ToxFMD Screened Chemistry™ Library (free for BM1 chemicals, others for sale): https://database.toxservices.com

2. If none are found, use GreenScreen List Translator via the Data Commons or ToxNot.
3. Assess results for data completeness and determine if more in depth assessments are necessary for any endpoints.
    a. If sufficient information is available to accurately and confidently distinguish between products, no further CHAs are necessary at this time.
    b. If information is not sufficient, complete QCATs as needed.
    c. If further information is needed, complete full chemical hazard assessments.

Criteria for Assessing Hazard in Food Packaging

Goal: Eliminate alternatives that are more hazardous than products with the chemicals of concern and distinguish between products with more moderate or even low hazard.

Showstopper criteria: Eliminate products with chemicals with PBT characteristics or classified as high for any of the Group I Human Hazards (carcinogenicity, mutagenicity, reproductive and development toxicity, and endocrine disruption). Chemicals with PBT characteristics are 1) very persistent and very bioaccumulating; 2) persistent, bioaccumulating and aquatically toxic; 3) very persistent and toxic; 4) very bioaccumulating and toxic. GreenScreen Benchmark 1 criterial can be used as a guide.

After products are eliminated due to showstopper criteria, the remaining alternatives can be compared. When comparing single chemicals, a direct comparison following the GreenScreen for Safer Chemicals method is appropriate. But we recommend using caution when using GS Benchmarks (BM). The GS BM system overly aggregates hazards into broad benchmarks that can impede informed decision making. It is better to compare chemicals based on the hazard summary table and to consider what is known about hazards tied to specific exposure routes.

When comparing whole products with chemical additives or chemical mixtures, it is useful to look at the individual chemicals and also to consider mixture rules such as those defined in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Mixture rules are particularly useful for hazards that can be ‘diluted out’ at the product level. For example, glacial acetic acid is very hazardous to handle, but when dilute in a product it is not hazardous. In contrast, we do not recommend applying mixture rules to PBTs and Group 1 hazards. Unlike with acids or bases, the hazardous properties do not go away with dilution, there is simply less of the hazardous chemical present.

General criteria for single-chemical alternatives:

1. Directly compare chemicals for GS Benchmark (BM) scores. Higher values are preferred over lower values. Rule out chemicals/products that score BM 1.
2. If the GS BM scores fall into the range of BM2, or if the chemical scores are equivalent, then the chemicals/products should be compared based on the specific hazards identified in the hazard tables.

3. Make sure to determine the exposure route that drives the hazard. This information will be needed for the exposure module. If people are exposed via the oral route but there are data only for dermal exposure, then we recommend treating that hazard endpoint as a data gap.

General criteria for whole products and mixtures as alternatives:

- Prefer alternatives that contain no GS BM 1 (GS LT 1) chemicals. That would include:
    - chemicals classified as high for any of the Group I Human Hazards (carcinogenicity, mutagenicity, reproductive and development toxicity, and endocrine disruption)
    - chemicals classified with PBT characteristics
- Prefer alternatives without data gaps for key hazard endpoints and for key exposure routes.

The purpose of each AA module is to make meaningful distinctions between the alternatives. In some cases, it may be desired to use a more sophisticated break-out of even highly hazardous chemicals, such as chemicals that score GS BM 1 and GS LT 1. It is possible to tell whether or not this is warranted by considering the typical lifecycles of the product and when these alternatives are used, particularly phases in which exposure cannot be controlled or cannot be predicted.

Driving innovation with AA:

1. Tradeoffs are likely between chemicals with different hazard profiles and varying amounts of data gaps. Some data gaps can be filled by qualified toxicologist using modeling tools and inference methods called ‘read across’. The goal is not necessarily to have perfect information, but to have sufficient confidence that the alternatives do not have undesirable hazard characteristics. Partner with innovators and manufacturers, unions and representatives of exposed communities to 1) drive demand for completion of research and development work to build comprehensive hazard profiles and 2) to inform decisions about tradeoffs in the face of uncertainty. Encourage manufacturers confident in the low hazard of the chemical ingredients they use to fund publicly available comprehensive CHAs.
2. Separate the chemical inventory of whole products into: 1) Water/grease-proofing performance additives 2) Non water/grease-proofing performance additives (e.g. UV stabilizers, whiteners); and 3) Chemicals used to make the base materials (e.g. processed wheat fiber, polymers such as PLA). This separates technologies used for water/grease-proofing from chemicals used for the base material and any other additives and can identify opportunities for innovation. For example, an otherwise preferable water/grease-proofing technology may be currently available only in products that also use an unacceptably hazardous UV stabilizer. This technology could be eliminated in the AA due to the UV stabilizer even though the rest of the chemistry is preferable. However, it may be possible to substitute or eliminate the UV stabilizer. By considering chemicals based on these functional uses, this opportunity is identified and encouraged.
3. Consider using AA to find alternatives for other chemical classes. For example, the Food Packaging Forum identified four phthalates commonly found in food contact materials (and in food) as top priorities for substitution (Food Packaging Forum 2018).
4. Develop information specific to processing aids and additives used in food packaging modeled after the Safer Choice Criteria for Processing Aids and Additives (US EPA nd). The US EPA Safer

Choice program treats processing aids and additives as a class. Similar guidance could be developed for processing aids and additives commonly used in food packaging materials.
5. Screen chemicals based not on hazard but also based on how they impact recyclability.

Comparative Exposure

Goal: After completing the hazard module, exposure is considered to reduce risk based on how the products are used.

The exposure module provides an opportunity to identify alternatives with lower exposure to chemicals that have moderate or low hazard properties, following the Commons Principles for Alternatives Assessment (2012) to minimize exposure. Preferred alternatives will not contain chemicals of high concern based on screening first with the hazard modules. However, most chemicals currently in use have some inherent hazards and it may be necessary to consider how the chemicals are used and their resulting exposure to people and the environment. We recommend starting with comparative exposure assessment rather than a full exposure assessment, focusing on exposure differences rather than exposure quantification. Some chemicals may be hazards in one life cycle stage due to their physical form rather than their inherent chemical toxicity. For example, powdered whiteners may be hazardous in the workplace but not bound within a polymer. It is not important what the total quantified exposure to a population is, but rather, the relative exposure between the alternatives.

Relevant exposure scenarios for food packaging include:

- Worker manufacturing food packaging
- Worker filling food packaging and providing it to customers
- Customer consuming food that was contained or stored in food packaging
- Worker handling food packaging end of life (e.g. recycling, composting, waste collection)
- Environmental exposure based on use scenarios
- Environmental exposure based on end of life of food packaging (e.g. landfill leachate, incineration products, unmanaged waste (litter))

As a first pass, we recommend assuming that any additives and residuals present in the food packaging product will result in maximum exposure (e.g. 100% leaches into food, 100% volatizes during manufacturing, 100% leaches from landfill). This is the worst-case scenario. If alternatives are considered acceptable under this exposure scenario, then no further work is necessary. For example, a product comprised entirely of chemicals of low hazard may be acceptable under this worst-case scenario. Any alternatives that raise concerns for worker, consumer or environmental health based on worst case scenarios should be evaluated further with modeling or testing. For more advanced assessment, we recommend an approach similar to that described in Greggs et al. (2018).

Worker Exposure

Workers in certain contexts are known to have higher PFASs serum levels, including workers at a PFASs production plant (Emmett, 2006), professional ski wax appliers (Freberg 2010), and workers at a textile manufacturing plant (Heydebreck, 2016). The extent of worker exposure to other constituents of food packaging will need to be estimated using modeling if testing results are not publicly available in the scientific literature. Personal protective equipment (PPE) may be considered but relying on protection from chemicals of concern by using PPE is not recommended.

Customer Exposure

It is important to carefully consider the potential uses and misuses of each alternative. Migration modeling or testing should mimic the most severe potential exposure condition, i.e. the highest temperature and longest exposure time anticipated. We recommend that initial considerations treat all food packaging equally, as if high temperatures and longest exposure times are expected. Food packaging only intended for cold or room temperature food contact that fails using these parameters could be reconsidered under more limited conditions and given a provisional pass.

Migration of food contact additives and other chemicals can be modeled mathematically. There are a number of different approaches to modeling including 1) deterministic or mechanistic models based on the physical chemical mechanisms driving the migration; 2) empirical models based on fitting modeling equations to actual data sets; 3) stochastic models that use probability distributions of migration; and 4) probabilistic models that take into account variables that occur with migration of chemicals and the probability of their occurrence. A useful summary of information on migration models and needs has been compiled by the Food Packaging Forum.

Migration of food contact additives and chemicals can also be tested directly. Performing migration testing would be more resource intensive. In a migration test, the food packaging is exposed to food or a food simulant for a specified period of time at a specified temperature, mimicking the most severe conditions of use. The US FDA provides detailed guidance for regulatory migration testing that can be followed (US FDA, 2007). Another option for gaining access to migration test data is to engage with manufacturers. All food contact materials must pass FDA criteria, which can include migration and compliance testing. By engaging with manufacturers, possibly under a Non-Disclosure Agreement (NDA) to protect Confidential Business Information (CBI), the results of this existing work may be shared with the assessors. This relies on the willingness of the manufacturers to participate.

Environmental Exposure

Comparative exposure of chemicals to the environment may be based on use patterns of the food packaging products and physical chemical properties of the chemicals (Greggs et al 2018). We recommend creating exposure maps to determine where environmental exposures may differ between products typically used in the same way. Exposure through end of life management should be linked to infrastructure currently available or reasonably anticipated to be available in Oregon.

Driving innovation with AA:

1. Partner with innovators, manufacturers, and unions to drive decreasing exposure across the product life cycle. Unions provide workers, who face increased exposure during manufacturing,

with a collective voice that can influence employers and reduce occupational illness and injury rates (Yi, 2011).

2. Consider how waste management infrastructure improvements and business models using food packaging products could meaningfully impact exposure results.

Cost and Availability

Goal: Ensure alternative products will be available in sufficient quantities to replace the products with the chemicals of concern and ensure that they are not cost prohibitive.

The cost and availability module ensures that alternatives are price-competitive and available in sufficient quantity. Inclusion of this module helps ensure that preferred alternatives can realistically be adopted by industry. Care should be taken to avoid biasing the module towards established technologies that have already been brought to scale. Cost should be considered across the life cycle of the products. For example, a reusable container may cost more up front but may become cost effective after a few uses.

Food packaging products are low-cost products and alternatives must have similar cost profiles to be readily adopted. We recommend researching the retail price of PFASs-containing products and the alternatives. However, this should not be used to eliminate alternatives within a reasonable cost range. Stakeholder engagement is recommended to help define a reasonable cost range; especially given regional variability, competition and expected cost reductions with scale. In addition, any product currently being used and purchased in the marketplace is at a reasonable price point for at least some users. Unfortunately, this criterion is not applicable to emerging products. It is worth acknowledging that the actual cost to businesses who provide take-out containers may be different from the retail price, but this information is not publicly available.

Food packaging products are fast-moving consumer goods, with a short lifespan and constant consumption. Assessors should discuss current production and the potential for future scaling of alternatives in order to understand the potential future costs and availability of these products for substitution. Availability of alternatives should be broken into functional categories, as defined in the performance module below, in order to understand if sufficient product(s) are available to match each function currently assumed by PFASs-containing food packaging.

Given Oregon's investment in the health of its people, its economy, and its natural resources, a more intensive full economic analysis is appropriate. Advanced cost assessment should include broader externalities such as societal impacts, human health, waste management, and litter. This would significantly increase the resources required for completing this module but would address other expenses that Oregon may incur. Cleaning up contamination is an expensive proposition so reducing the amount of toxic chemicals used and disposed of in Oregon may impact future costs. Costs from health impacts from PFASs exposure and exposure to other hazardous chemicals in alternatives would also be considered in a full economic analysis.

Performance

Goal: Ensure alternatives function for the desired application and that they meet minimum requirements.

The performance module is designed to ensure that alternative products will perform the same core function as the chemical or product of concern. Inclusion of this module helps ensure that alternatives that do not work are not recommended based on the AA. We recommend using stakeholder input to define a suite of performance criteria for different uses and to identify available performance metrics. We recommend a four-step process to this module, with stakeholders engaged at every stage:

1) Define the functions of currently-used PFASs-containing food service ware
2) For each function, define minimum/showstopper and stretch criteria and metrics
3) Match each product to appropriate function(s)
4) Assess products according to function

Actively engaging stakeholders in this module will improve criteria and metrics, as well as acceptance and adoption of the results of the alternatives assessment. By providing a voice to those who use food packaging containing PFASs, the assessors ensure that their concerns and needs are represented. If only users who have already substituted with alternatives are included, key functional parameters that are not covered by currently available alternatives may be overlooked and not considered, leaving these users without any functional alternatives. Diverse users should be engaged, including restaurants, food trucks, cafeterias, caterers, hospitals, schools, prisons, and consumers. For this module, in particular, it is vital that the assessors do not proceed without consulting stakeholders.

Food service ware covers a variety of functions, ranging from holding low-density room-temperature dry food to high-density hot and greasy liquids. The minimum water and grease resistance and strength of a bowl used to hold hot, greasy soup is different for a bowl used to hold cold, undressed salad. While a single PFASs-containing product may be capable of handling these diverse functions, multiple alternative products may be necessary to handle all of the same functions. It will be important to consider situations in which products currently using PFASs are overengineered for the function they provide.

Products are overengineered when they are designed to be more durable or have additional performance characteristics beyond what is necessary. In some cases, overengineering provides an additional safety factor or permits for minor manufacturing defects without compromising the product. overengineering is not an issue when it does not result in compromise in other modules. However, overengineering can also result in erroneously concluding that no functional alternatives are available due to the extraordinarily high-performance criteria.

One example comes from the use of PFASs in durable water repellents (DWRs) for apparel (Schellenberger, 2019). DWRs provide water and stain proofing to apparel. While alternatives to PFASs in DWRs for water proofing are commercially available today, many brands do not believe they are sufficient due to the lack of robust stain resistance. A detailed analysis of actual performance requirements and consumer expectations revealed that stain proofing is unnecessary for many garments. Outdoor apparel users are primarily concerned with water-proofing. These users ranked stain resistance as the lowest priority in purchasing decisions. One response highlighted that stain repellency is “not crucial to preventing hypothermia on the mountains” (Schellenberger, 2019, pp. 140-141). The use of PFASs in outdoor apparel results in overengineering the product by conferring additional performance benefits that are not central to users’ needs or expectations. Before PFASs were recognized as chemicals of concern, this was not problematic.

Overengineering may occur in food packaging as well. For example, overengineering may result from the use of the same packaging for diverse food products. A restaurant may use the same bowls for hot and greasy soup, cold salads, and dry bread. The bowls in this example are overengineered for the cold and dry uses but needed for the hot and greasy soup. The bowls may be overengineered for all uses if they are sufficiently durable and leak-proof to last longer than about a week while filled.

Performance criteria should include showstopper limits and stretch criteria. Showstopper criteria are used to eliminate products that simply do not perform. For example, soup bowls that leak or clamshells with low tensile strength that collapse when loaded. Stretch criteria are used to distinguish between products that perform above and beyond their basic function. Stretch criteria should not be used to eliminate any product that meets the minimum criteria. Stretch criteria can help identify products that may be overengineered for a given function, but that overengineering is useful in reducing the number of different containers a given business must have available for use. It may be convenient to be able to use the same bowls for hot and greasy soup as for dry bread.

This module can be made less resource intensive by setting the minimum criteria for performance as the product being available on the market. Any product currently being used and purchased on the market must meet at least some user requirements. Emerging products cannot be assessed using this method and will require further consideration or comparison to existing alternatives. Another strategy to reduce resources necessary for this module is to limit the number of different functions assessed. Stakeholder input should be used to identify the most common and widespread functions. Stakeholders could also help identify where no PFASs-free alternatives are considered to be available.

This module can be made more resource intensive by performing actual testing of products to determine if they meet performance criteria. TAPPI, the Technical Association of the Pulp and Paper Industry, maintains standards and methods for used in the measurement, evaluation, and description of pulp, paper, and related products. While food packaging materials comprise more than just pulp and paper, these methods may be useful for paper-based alternatives and potentially for non paper-based alternatives as well.

The Kit Test (TAPPI T559) describes a method for measuring the degree of repellency/anti-wicking of a paper or paperboard treated with PFASs (TAPPI). It involves testing the treated paper with a series of liquids of varying surface tension and viscosity and observing which remains on the surface of the paper without causing failure. It is unknown if this test would be appropriate for alternatives, such as barrier coatings, mechanical treatments, or alternative materials.

The Foodservice Packaging Institute (FPI), is a North American trade association for the foodservice packaging industry that provides information on some test methods on their Resources webpage (https://fpi.org/Resources), including:

- Harmonized hot oil test for printed, finished foodservice products. This test exposes the use side of the product to hot corn oil containing red dye for 20 minutes. The oil is then removed with a spatula followed by a paper towel, after which the back side of the product is immediately examined for red marks.
- Leak test for poly coated hot cups. This test exposes the inside of the cup to a mixture of coffee and wetting agent (approximately 0.3% Triton X-100 final) for 20 minutes, during which the cups are inspected for leakers.

FPI also produces a rigidity tester for testing rigidity of single-use foodservice packaging products and maintains a standard operating method for its use.

While testing of products would add value to the resulting alternatives assessment, it will also result in an increase in cost, both time and resources. Testing may be necessary to overcome bias and increase adoption of alternatives. We recommend consulting with relevant stakeholders before committing to testing. It may be that no single test is sufficient to cover all stakeholder concerns.

Social Impacts

The goal of the social impact module is to ensure that the product(s) brought forward by the alternatives assessment do not result in unduly shifting a burden from one community of people to another. It is important to broadly consider the full life cycles of the products and to identify relevant stakeholders throughout. While the focus of this module is social justice, environmental justice organizations are critical in connecting social justice concerns with relevant impacts.

Stakeholder engagement is critical for this module. Stakeholders will identify burden-shifting and impacts that are not readily apparent to the assessors. Stakeholders should include the Oregon Environmental Justice Task Force, and representatives from OPAL Pdx and Beyond Toxics, two non-profits focused on environmental justice in Oregon, as well as representatives from environmental justice communities in Oregon, such as the Coalition of Communities of Color. Environmental justice communities in Oregon include racial/ethnic communities, low-income communities, tribal communities, and underrepresented communities (such as youth, elderly, or mental disabled) (Oregon Environmental Justice Task Force, 2016). While we specifically recommend these stakeholders for a focus group on the social impact module, it is necessary to include them in stakeholder discussions throughout the project in order to ensure that social and environmental justice is fully integrated in all modules of the alternatives assessment.

We recommend following Level 2 of the IC2 Guide (2017) for this module. This includes a consideration of impacts in Oregon during the use and end of life of the products and impacts globally from the manufacture of the food packaging products.

Suggested showstopper criteria for this module include:

- Use of child labor to manufacture or transport product
- Use of forced labor or slavery to manufacture or transport product
- Extraction of resources that contribute to unhealthy societies such as support of unethical military actions, genocide, etc. (e.g. conflict minerals)
- Extraction of resources or manufacturing that contributes to environmental degradation (e.g. unsustainably harvested palm oil, over-extraction of key resources).

We strongly recommend working closely with stakeholders to develop appropriate showstopper criteria for Oregon.

Results from this module may be used to alter assessment results from other modules. For example, if recycling of the product occurs primarily at an overseas plant that uses child labor, the product may be considered merely potentially recyclable as opposed to realistically recyclable.

Driving innovation with AA:

1. Some of the harmful impacts identified in this module involve practices that are broadly considered unacceptable by the average American consumer, such as child labor, slavery, shifting burdens to vulnerable populations, and genocide. Documentation of these practices could be shared with relevant stakeholders, such as environmental justice organizations and advocacy groups, in order to develop campaigns that lead to the voluntary elimination of these practices. Simply including the information in a report may not call it to the attention of the appropriate organization, and simply sharing with media is insufficient to generate the long-term support necessary for effective social change.
2. Guidance exists for companies interested in ensuring they are acting in a socially responsible manner. Companies that perform poorly in this module could be directed to existing resources:
    - ISO 26000 provides guidance for businesses and organizations to help them translate principles into effective actions and describes best practices relating to global social responsibility.
    - The SA8000® standard is a certification standard based on conventions of the International Labour Organization, the United Nations, and national laws.
    - The Global Reporting Initiative’s Sustainability Reporting Guidelines include guidance for reporting on issues such as climate change, human rights, and corruption.

Materials Management

Goal: Reduce impacts on natural resources across the life cycle. Preserve natural capital by eliminating waste and maximizing value recovery from products after use.

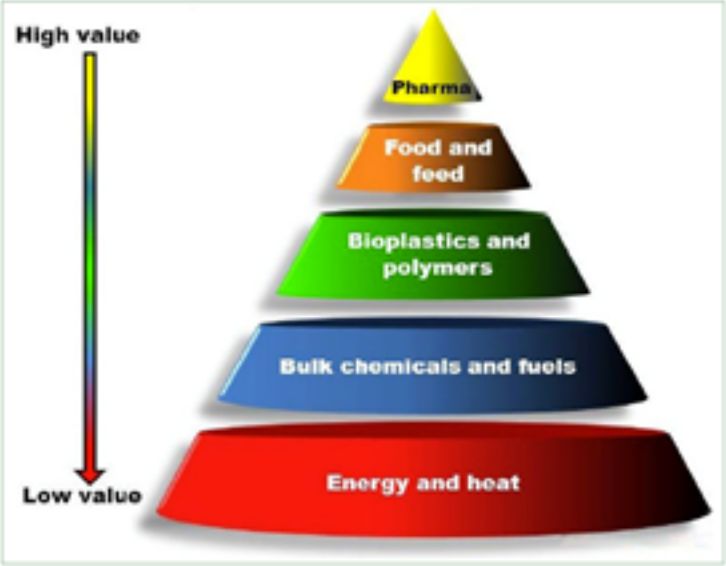
Materials management considers how the selection of different products may impact natural resource preservation/depletion and the potential for eliminating waste and maximizing material recovery value from products after use. It considers both the quantity and quality of wastes and how chemicals in materials can impact opportunities for recycling, composting, and other forms of recovery. It allows for a consideration of compatibility with, and progress towards, a circularity economy and identification of innovation needs. These parameters must be balanced with an assessment of measured impacts from the other modules, such as the LCA impacts in the Life Cycle Thinking module.

Sustainable materials management of food packaging products is necessary. Ideally, a circular material flow system will be efficient and will minimize negative impacts across the life cycle. Tools such as life cycle assessment (LCA), discussed in the next section, are valuable for assessing efficiencies and life cycle impacts. However, LCA does not typically address impacts such as propensity of a product to become litter, the flexibility of some products to undergo different waste management treatment processes, and geographical differences in societal waste management practices. Care must be taken to avoid focusing on single attributes of materials such as recyclability, compostability, or circularity that may drive undesirable tradeoffs across the lifecycle. At the same time, overall life cycle benefits should not result in tradeoffs that are unacceptable to a society. LCA is always useful for checking assumptions and identifying hot spots and opportunities for improvement and innovation.

Feedstocks: Products are not using sustainable feedstocks if they are based on 1) non-renewable, non-recycled/recyclable resources, 2) feedstock that degrades or consumes renewable resources faster than they can regenerate, or 3) materials that degrade the environment or compete with food production.

Sustainable materials management provides guidance for using fewer materials and materials that are reusable or recyclable numerous times. There is a general preference for recycling of ‘permanent’ materials, i.e. a material whose “inherent properties do not change during use and, through solid-liquid transformation, it can revert to its initial state” (Conte, Dinkel, Kägi, & Heim, 2014, p.12). Permanent materials used in food packaging include glass and metal, while non-permanent materials include paper and some plastics. Recycling of non-permanent materials typically requires input of virgin materials to overcome the degradation or impurities of the recyclate (Geueke et al., 2018).

Bio-based feedstocks are typically considered as having positive attributes as they are not based on fossil fuel resources. However, actual decreases in fossil fuel usage are challenged by LCA (Mistry et al., 2018). When bio-based materials are used, this usage may compete with other, possibly more valuable uses. The Biomass Value Pyramid in Figure 5 depicts a cascading approach to preferred biomass use with the highest priority given to the uses at the top of the pyramid (Devaney, Henchion, & Regan, 2017). Assumptions about key attributes should be verified with life cycle assessment.



Source: Peter Westermann, taken from Lange *et al.* (2012: 88)

Figure 5. The Biomass Value Pyramid shows a general preference for bio based feedstock usage: Pharma > food & feed > bioplastic & polymers > bulk chemicals & fuels > energy and heat (Lange et al., 2012).

The following rules of thumb may be useful in selecting feedstock for materials. But assumptions should be checked using LCA:

- When comparing like materials, use less material
- If based on renewable feedstock, prefer products based on agricultural waste versus renewable materials grown for use in food packaging. Prefer feedstock that are derived from sustainably managed crops, that are locally sourced, and that do not compete with “higher” uses (i.e. social, ecological, or food production value on the local, regional, and/or global scale).
- If based on recycled content, prefer alternatives that:
  - Use more recycled content over those that use less recycled content (when comparing like materials)
    - Use virgin feedstock within a defined material flow system that will result in the use of recycled content on the next cycle
    - Use ‘clean’ recycled content

Manufacturing:

Prefer alternatives that minimize consumption of resources and the generation of wastes during manufacturing. Prefer alternatives that do not require hazardous processing aids or additives that could interfere with material recovery.

Use:

Prefer alternatives with optimized product/packaging design for cleaning, reuse or recycling as well as other life cycle benefits (e.g. decreased packaging mass).

End of life:
The product’s compatibility with preferred end of life options requires that the infrastructure exists to collect, sort, and process the product in that manner. Alternatives that can be composted in industrial facilities cannot provide their intended benefits when there are no industrial composting facilities in the region, or if facilities will not accept food service ware. Alternatives that can be recycled cannot provide their intended benefits when collection, sorting, and cleaning infrastructure is not available; or if a recyclable material is not wanted for recycling when contaminated with food. The possibility (or likelihood) that the packaging product may end up as litter must also be included in the assessment. Neither commercial compostability nor recyclability are beneficial if the product is frequently littered.

Products should include having a plan for recovering and recycling the material after use that accounts for regional differences. The plan may take advantage of publicly accessible waste management infrastructure or it may involve a closed and privately managed materials system based on product stewardship. In additional to optimizing design to account for other life cycle impacts, product design should be optimized for recovery and recycling of the material and instructions should be detailed, going beyond labels that say, ‘please recycle’. For example, Green Blue Institute developed the How2Recycle Labeling program to optimize proper product and recycling management of packaging (How2Recycle Program, 2018). Unfortunately, this system used national recovery averages and may not hold up well for some regions in Oregon; greater specificity should be encouraged. Products managed with product stewardship like this should be preferred.

Some products may be suitable for multiple waste management/material recycling pathways. Products should be designed to facilitate recycling and other forms of material recovery. For example, some chemical additives may be benign from the toxicity perspective but may interfere with successful recycling. Such additives could range from certain fillers to colorants. Products should also be designed to minimize negative impacts from all feasible waste management pathways. For example, some additives (i.e. halogens) may transform into problematic pollutants when incinerated. The potential for toxics to contaminate the end of life pathway must be a consideration.

Prefer alternatives that generate less waste; particularly those that generate less hazardous waste / less waste with negative impacts. Avoid waste generation first, and secondly optimize material value recovery. Ideally products will be designed to account for regional differences in waste management infrastructure, allowing for flexibility in waste management options and reducing impacts from all likely waste management pathways. Prefer alternatives that do not contain chemicals that will interfere with end of life pathways, or that may contaminate end of life pathways.

Prefer alternatives that are recyclable, particularly those that are up-cyclable (can be recycled into similar or higher value products) over those that are only down-cyclable (can be recycled only into lower value products); can be recycled multiple rounds; and that are realistically recycled. Keep in mind available infrastructure and necessary preparation for recycling; food service ware is commonly contaminated with food waste and cannot be realistically recycled using available infrastructure. Check assumptions of recycling benefits using life cycle assessment (see Life Cycle Thinking).

Prefer alternatives that are biodegradable; particularly if they biodegrade in a way that has less of an impact if unintentionally ‘leaked’ out of the waste management system or littered. For example, paper fiber degrades far more quickly in wet environments than plastic. Litter is a worst-case scenario and products should not be designed or marketed in a way that might encourage littering. Nevertheless, prefer alternatives that are home/backyard compostable and marine degradable if available.

Products that are industrially compostable may be preferable in a region that encourages industrial composting. However, due to the lack of acceptance of food packaging at local Oregon composters, this attribute should be weighted lower than biodegradability and recyclability. For regions that encourage industrial composting, prefer alternatives that have certifications and/or 3rd party testing verifying their biodegradability/compostability. These alternatives should not degrade the resulting quality of the compost. Rather, they should enhance the resulting quality of the compost and help capture desirable compost feedstock (e.g. food scraps). See Test Methods and Certifications section below.

Prefer products managed under product stewardship principles including product takeback. At a minimum, products should come with clear instructions for managing them after use. Instructions and product design should both support correct sorting (e.g. redesign an item so that users can recognize it as a different material and help to ensure that it is not mis-sorted into the wrong recovery stream).

Metrics look at the % of each product matching the preferred attribute (e.g. % recycled content). When considering actual rates of disposal using different EOL pathways or comparing products based on available infrastructure, assign percentages of product to each disposal pathway for comparison, as well as comparing them based on their likelihood of undergoing worst-case waste disposal scenarios.

Opportunities to Mitigate Negative Impacts and Advance Sustainable Materials Management

Engage stakeholders to understand how they use the products and the waste management systems that exist in their regions. Collaborate with them to identify opportunities to mitigate negative impacts and advance circularity. What are different usage scenarios for these products? Could changes in packaging design, materials, or weight mitigate negative impacts? Are there opportunities to advance circularity by utilizing less virgin material? Focus on major hotspots for each product technology type in addition to differences between products of similar type. How might a different business model mitigate impacts?

For example, Taco Time Northwest in Washington State converted to 100% commercially compostable packaging in 2014. Prior to that, 90% of their waste had been going to landfill due to contamination of the recycling bin at their restaurants, despite intended sorting into garbage, recycling, and compost (Campbell, 2014). By switching to 100% commercially compostable packaging, Taco Time Northwest was able to create a closed and controlled waste management system. A restaurant with complete control over the packaging offered and waste management streams available can mitigate negative impacts from mis-sorting by simplifying the process.

An innovative alternative to disposable food take-out containers has been embraced by some food trucks and restaurants in downtown Portland (Baker, 2018). The GO-Box is food take-out packaging as a service. Reusable polypropylene containers are distributed to participating businesses. Consumers sign-up on an app, and check-out a container when they pick up food. Consumers then return the container to participating locations, after which GO-Box employees pick up the containers, wash them, and redistribute them. Life cycle impacts are reduced further by using bicycle transportation (Maus, 2018).

Driving innovation with AA:

1. Available infrastructure for end-of-life management determines the relative preference of different end-of-life options. Outside of Oregon, many groups, including MN and NY, prefer compostable food packaging in part because contamination by food waste is not an issue with composting, as it is with recycling. What can be done to prevent mixing of non-compostable packaging with fully commercially compostable packaging? Are there improvements to how we collect and process materials for recycling that would elevate recycling's position relative to composting? Can novel recycling methods be developed that are compatible with food waste? We recommend ongoing engagement with composters, recyclers, waste collectors, and manufacturers who use recycled material to discuss the benefits and drawbacks of allowing food packaging materials in industrial composting, and the possibilities of increased recycling.
2. Are there unused opportunities to utilize waste food packaging products? Partner with innovators and manufacturers to spur development of opportunities to add value to these underutilized resources.
3. Is there an opportunity for a disruptive innovation to replace a product's function? Can single use, disposable food packaging be avoided? Convene users of the product with innovators to discuss alternative methods of achieving the product's function. The best alternative products may not be products at all. They may be innovative business models or wisely engineered reuse or recovery programs.
4. Could use of reusables be promoted by requiring restaurants and food trucks to charge a fee for disposables, similar to plastic bag fees? Convene a focus group to discuss the possibilities.

Test Methods and Certifications

Multiple methods are used to test and indicate the type of degradability/compostability associated with materials and products and thresholds for contaminants. In this section, we review 1) test methods for assessing environmental biodegradability, and 2) standards and certification programs that assess material degradability. Some of these methods are useful for identifying food packaging products that are PFAS-free, even if biodegradability is not the priority.

We summarize information below on organizations that have developed standards and certifications for degradability and compostability (Figure 7).

In addition, we evaluate the standards for whether or not they consider PFASs (Table 6).

Appendices A, B and C provide more detailed information on each test method, standard and certification program.

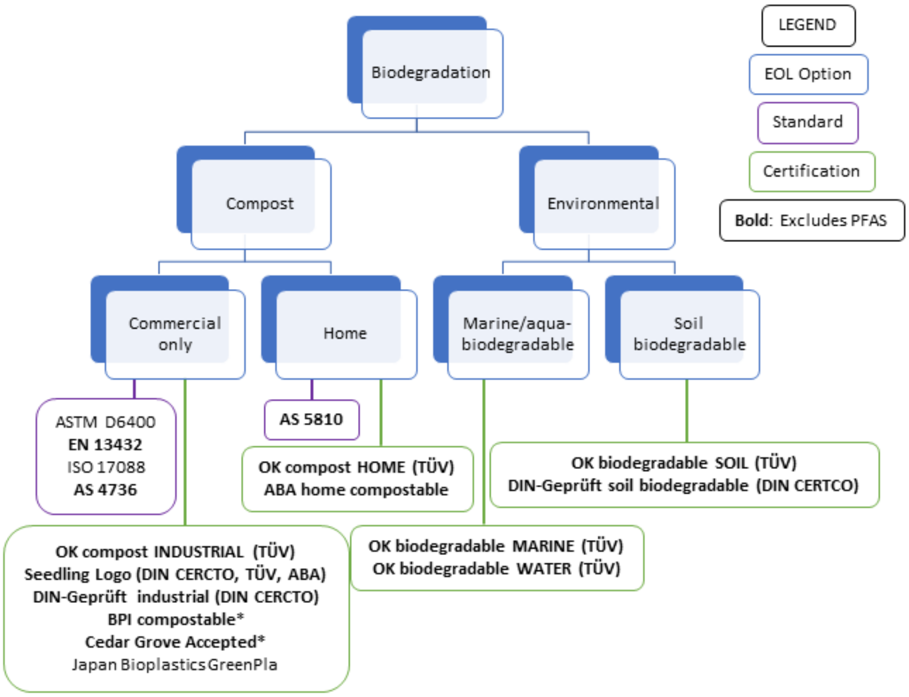


Figure 6. Standards and certifications for biodegradation end of life pathways for food packaging.

Standards and certifications in bold (ASTM D6400, ISO 17088, and Japan Bioplastics GreenPla) do not include a 100 ppm fluorine limit. Certifications in italics (BPI compostable, Cedar Grove) are phasing in a 100 ppm fluorine limit by 2020.

Table 4. Standards and certifications for compostable and biodegradable food packaging and PFASs considerations (via 100 ppm fluorine limit).

Standard		**Excludes PFAS (100 ppm fluorine limit)**
ASTM D6400		N
ISO 17088		N
EN 13432		Y
AS 4736		Y
Certification	**Related standard(s)**	**Excludes PFAS (100 ppm fluorine limit)**
BPI	ASTM D6400	N through 2019, Y post-2020 on new items, renewals, and existing inventory
Cedar Grove	ASTM D6400	N through 2019, Y post-2020 on new items and renewals
TÜV AUSTRIA OK compost INDUSTRIAL	EN 13432	Y
TÜV AUSTRIA, OK compost HOME	mod. EN 13432	Y

Certification	**Related standard(s)**	**Excludes PFAS (100 ppm fluorine limit)**
TÜV AUSTRIA, OK biodegradable SOIL/WATER/MARINE	varies	Y
TÜV AUSTRIA, Seedling Logo	EN 13432	Y
Standard		**Excludes PFAS (100 ppm fluorine limit)**
DIN CERTCO, Seedling Logo	EN 13432	Y
DIN CERTCO, DIN-Geprüft test mark for industrial compostability	EN 13432	Y
ABA, Seedling Logo	AS 4736	Y
ABA, home compostable	AS 5810	Y
JBA, GreenPla	custom	N

In determining if the product is compostable, a functional standard must define the conditions under which it degrades include the temperature needed and the time required for composting. The standard must also distinguish between fragmentation/disintegration and true biodegradation. IUPAC defines *disintegration* as fragmentation to particles of a defined size, with the limiting size typically defined by sieve conditions (Vert et al., 2012). On the other hand, *biodegradation* is degradation caused by enzymatic process resulting from the action of cells, which has been modified from former definitions by the exclusion of abiotic enzyme processes (Vert et al., 2012). The separation of these processes is clearly demonstrated in most plastics, which first fragment with physical processes into smaller and smaller plastic pieces, increasing the surface area and availability of molecules for biodegradation. The fragments may then biodegrade into minerals, water, and carbon dioxide over time.

While the stability of the non-fluorinated moieties in PFASs vary, the perfluoryl moiety of PFASs resists biodegradation and is very stable (Liu, 2013). Some PFAS classes, like the perfluorylalkyl acids (PFAAs), a class that includes PFOS and PFOA, are resistant to microbial biodegradation and are therefore considered recalcitrant (Liu, 2013; Ochoa-Herrera, 2016). Some PFASs undergo primary degradation whereby the parent compound degrades into a daughter compound that is recalcitrant. PFAAs are common biodegradation products of other PFASs (Liu, 2013). As the food packaging material breaks down, some PFASs may bio-transform into other PFASs, but the expectation is that the overall PFAS burden remains constant. PFAS levels in compost from facilities that accept residential and commercial food waste and compostable food packaging and service ware are higher than PFAS levels in compost from facilities that only accept yard waste (Lee & Trim, 2018). PFASs are taken up from soil by crops, and have been shown to accumulate in edible portions, though the bioaccumulation of PFASs depended strongly on PFAS species and concentration, soil properties, and the type of crop (Blaine, 2013).

Some certifications could be used to indicate products that do not contain PFASs. The European standard EN 13432 limits PFASs by limiting fluorine content to 100 ppm. This would exclude intentionally added PFASs for water/grease resistance. Certifications based on EN 13432, like TÜV AUSTRIA’s OK compost INDUSTRIAL certification, should also appropriately exclude PFASs-containing food packaging products. The ASTM standard D6400 does not consider fluorine content and would permit PFASs. Certifications based on D6400, like BPI's compostability certification, permitted PFASs (CEH, 2018). However, BPI has adopted the 100 ppm limit from EN 13432 and is currently phasing it in with full adoption planned beginning in 2020 (BPI, 2017).

Life Cycle Thinking and Life Cycle Assessment

Goal: Holistic and quantitative comparison of products for impacts across defined life cycles,

The overall goal of the Life Cycle module is to take a comprehensive view of product impacts across the life cycle, to identify opportunities for innovation and improvement, and to avoid burden-shifting. Life cycle thinking is not exclusive to life cycle assessment. It is necessary for every module in an AA. For example, hazard must be addressed during manufacture, use and end of life. The same is true for exposure, social impacts, etc. Therefore, we do not recommend a separate module for life cycle thinking. It is germane to every module.

The goal of this module is to present a more holistic picture of the product system. We recommend a Level 3 assessment with LCA following ISO 14040 guidelines. Life cycle assessment is important for identifying hot spots, particularly between different types of technologies (e.g. reusable plastic packaging versus commercially compostable fiber packaging). Identifying hotspots can help to inspire ideas about how to mitigate impacts from those hotspots. For example, while bio based does not guarantee life cycle benefits, some bio based feedstocks have more benefits than others depending on requirements for energy, water, pesticides, etc. And in LCA, use of agricultural wastes can result in life cycle benefits because the impacts associated with the crop are not ascribed to the wastes. LCA is not likely to be the best tool for comparing products of similar design with minor differences, such as different versions of a functional chemical additive; unless differences result in different use or end of life pathway options.

LCA is also important for checking and verifying assumptions about environmental impacts associated with different product attributes. (Mistry, Allaway, Canepa, & Riven, 2018). A summary of challenges to assumptions about health and environmental benefits associated with common sustainability related attributes follows.

Challenges with Attribute-based Assessments

In a recent review of the literature, results of LCAs of packaging and food service ware were analyzed (Franklin Associates, 2018). They researchers reviewed LCAs that included comparisons relevant to four material attributes commonly associated with decreased environmental impacts and presumed to advance circularity. OR DEQ further summarized this work and made recommendations on the utility of each attribute, summarized below (Mistry et al., 2018):

- Bio-based - limited utility for predicting reduced environmental impacts, generally preferable/mixed.
    - Production of all current bio-based materials involves combustion of fossil fuels

        - Comparing bio-based and fossil fuel-based for the same material: Bio-based almost always reduces fossil fuel use.
        - Comparing bio-based against non-bio-based: Results are mixed.
    - Often conflated with other attributes, like compostable or biodegradable.
    - Tradeoffs exist with other impacts such as acidification and eutrophication.
    - Recommends calculating energy required for materials instead of using bio-based as a metric.
- Compostable - poor indicator
    - Often results in higher environmental impacts than non-compostable.
        - Higher burdens associated with feedstock production.
        - Low value recovery in composting compared to other options, e.g. recycling.
    - Poor user compliance and poor certifications/standards.
        - Certified compostable materials do not necessarily compost well in existing facilities.
        - Acceptance of compostable materials that appear similar to common non-compostable materials increases contamination of the compost.
        - Current certifications and standards are insufficient at managing emerging chemicals of concerns, like PFASs. See the section, *Test methods and thresholds used and indicate the type of degradability/compostability associated with materials and products,* for details.
        - Compostable may be confused with environmentally biodegradable, increasing litter.
    - Recommends against using this attribute in isolate, and instead using LCA.
- Recyclable - poor indicator
    - While recycling is typically beneficial when compared with alternatives like landfilling, the attribute of recyclable covers a distinct concept: Does use of readily recyclable materials lead to lower environmental impacts?
    - Mixed results for different packaging materials and tradeoffs do not easily fit into patterns; limited studies of food service ware show lower impacts but avoided key issue of food contamination.
    - Increasing recycling rates typically decreases negative impacts but requires infrastructure investment and user compliance.
    - Recommends against using this attribute in isolation, and instead using LCA.
- Recycled content - poor indicator
    - Once a material is selected, increasing recycled content almost always reduces negative impacts.
    - When comparing different materials, recycled content does not necessarily track with reduced impacts.
    - Recommends first optimizing profile via the use of materials and formats with the lowest impacts, then increasing recycled content to minimize negative impacts.

Driving innovation with LCA: LCA should be used to identify hotspots associated with different product types and to verify assumptions about differences between products based on their attributes. How could these hotspots be addressed using currently available technology? What research and development is necessary to mitigate the impacts? It can also be used to identify truly disruptive technologies that provide overarching life cycle benefits versus incremental improvements. For example, LCA could be used to verify whether or not a reuse model has more life cycle benefits than recycling; and how many reuse cycles would be necessary to provide those benefits. Likewise, it can be used to demonstrate incremental improvements within a technology such as demonstrating benefits from increasing amounts of recycled content.

Step 6: Take Action

Integrating with Existing and Ongoing AA Efforts

We recommend coordinating with existing and ongoing AA efforts to address PFASs and other chemicals of concern in food packaging and communicating with the other groups engaged in AA to avoid duplication of efforts. Ideally, each AA group would assess the same products but use different modules. This ensures that the results will be comparable and complementary, and that work is not duplicated unless necessary. However, we know that Washington State will conduct an AA in 2019 that is limited to consideration of hazard, exposure, cost & availability, and performance; and that the scope of products to be considered will be established by the assessor in collaboration with WA Department of Ecology (WA DOE). Nuances to the WA State law banning PFASs may require that the assessors narrow the focus of the products evaluated in the AA to demonstrate the availability of alternatives to key PFASs containing products.

OR DEQ can build on the WA AA work (beginning Fall 2019) to update this Roadmap and determine what additional work should be done. In order to build on an existing alternatives assessment of food packaging, the relevance, quality, breadth, and depth of the assessment must be ascertained. The quality of the assessment is tied to how well the criteria help to discriminate between products and to identify a preferable product as defined by the scope of the AA. Did hazard criteria overlook key endpoints, such that certain types of regrettable substitutions may not have been caught? Did hazard criteria overreach, resulting in the elimination of products that may be otherwise preferable? Did performance criteria consider all relevant use cases, or were some overlooked? Were performance criteria too stringent, promoting overengineered products in order to excel in the performance module? And so on. For any area in which criteria were too lax or too stringent, it may be necessary to re-evaluate the decision on which products are preferable, or to re-assess the module.

If reevaluation or reassessment of a module is necessary, and the existing AA used a sequential decision analysis method, it may be necessary to assess products that were dropped early. The goal is to ensure that the results are relevant to Oregon. Oregon’s regulations and infrastructure may result in the use of different decision criteria than those used for other regions.

OR DEQ should first determine if all products of interest have been assessed; and if not, which products should be added. Are these products unique, using a different base material or grease/water resistance chemistry than the products that have been assessed? If so, are these products likely to be preferable? Are there known showstopper criteria that these products fail? If necessary, complete a cursory screening assessment in select key modules. From there, OR DEQ will need to determine if the additional work of assessing the additional product(s) is worth the cost.

Implementation Plan

An AA report is a snapshot in time and should be accompanied by an implementation plan. The plan should include strategies and resources for ongoing identification and evaluation of emerging alternatives, for driving and measuring adoption of alternatives, and for integrating other important information. Novel information may emerge over time including new toxicology studies, changes in economics, and new waste management methods. Oregon should consider collaborating with other governmental agencies and key stakeholders to create an implementation plan for the proposed AA. Additional recommendations for next steps towards setting the stage for substitution include:

- Publicly state Oregon's priorities for PFASs free products. For example, as with a waste hierarchy, and consistent with OR's materials management vision, OR DEQ could state that its priorities are 1) to avoid products with hazardous chemicals to which people and the environment will be exposed across the product life cycle and 2) to promote a circular economy that eliminates waste at the source and recovers materials at the highest possible value for reuse. This should clarify how existing statements on sustainability apply to food packaging.
- Develop promotional and educational materials for diverse users explaining the issue and describing how to select PFASs-free alternatives.
- Identify additional classes of chemicals to eliminate. For example, ortho-phthalates have been identified by the Food Packaging Forum as a priority for replacement in food packaging.
- Create or revise procurement policies to purchase PFASs-free food packaging. Appendices A,B and C in this report provide detailed information, including pros and cons, of test methods, standards and certifications. Some certifications exclude PFASs and others do not. The European standards based on EN13432, generally exclude PFASs due to a 100 ppm fluorine limit, while US standards do not. However, some US standards (i.e. BPI certified compostable) are being updated to address this issue.
- Identify products as PFASs-free by:
    - Testing and making a list of PFASs-free options available in Oregon.
    - Using the CEH list as a starting point, but keep it updated, as products change over time.
    - Using compostability/biodegradability certifications such as TÜV AUSTRIA Seedling Logo or post-2019 BPI compostable that also include limits for fluorine.
    - Consider supporting or developing a certification for simply PFASs-free products, as the compostability/biodegradability portion of these certifications is not relevant to Oregon currently.

Adoption of safer, more sustainable alternatives is a process that requires changes in behaviors by key stakeholders. Identifying viable alternatives is only the first part of an ongoing initiative. Collaboration can include identifying goals and priority targets; agreeing on criteria for inclusion on green lists; and gathering information about stakeholder's values to improve adoption rates and outcomes. As goals become more specific, a program that encourages targeted behavior through incentives will form. The behaviors desired determine the overall learning objectives that will drive change and that shape the intervention activities required. It is important that OR DEQ set outcome metrics at the start of the AA process to evaluate whether change is occurring and to identify ways to improve its implementation strategy to achieve ongoing goals. In this way, OR DEQ and its collaborators can improve human, environmental, and economic health while avoiding unintended consequences, perverse incentives, or regrettable substitutions.

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Appendix A: Test Methods for identifying PFASs in Products

Most PFAS methods can be divided into 1) extraction, concentration, or derivatization, 2) separation, and 3) detection and quantification. While these steps are linked and are not interchangeable between methods, certain steps are commonly shared. For example, HPLC is the most common separation method.

Regardless of the test method employed, it is important to minimized fluorinated chemical contamination and analyte loss and ensure standards are well characterized (Martin et al., 2004). Personal protective equipment, such as insect repellent necessary for collecting certain environmental samples, and personal care products may contain PFASs that could contaminate samples (Bartlett & Davis, 2018; Fujii, Harada, & Koizumi, 2013). Teflon^{TM}, comprised of PFASs, is commonly used in laboratory supplies and equipment, such as stir bars, sample container caps, pipette tips, tubing, tape, seals, septa, chemical containers and caps, and even seals and linings within analytical equipment and instruments (Kempistry, 2018). Post-injection contamination on HPLC systems, presumably due to internal fluoropolymer components, is common (Martin et al., 2004). Glassware should be avoided due to potential analyte loss due to adsorption (ISO 25101:2009). All sample containers should be rinsed thoroughly with water and methanol prior to use and should be checked for possible background contamination before use (ISO 25101:2009). Commercially available standards vary in purity and isomer profiles, confounding accuracy as well as inter-lab comparisons (Martin et al., 2004; Valsecchi, Rusconi,& Polesello, 2013). An analysis of commercially available standards revealed that purity ranged from 86% to >= 97%, which could potentially cause a significant over-estimation of PFASs in samples (Naile, 2010). Additionally, not all labeled standards had the same response as unlabeled versions, depending on the matrix, and the use of primarily linear-only standards could result in underestimation of PFASs in samples (Naile, 2010).

Standard Test Methods

A small selection of standard test methods for detection of PFASs exist, but they are limited by their use of liquid chromatography with tandem mass spectrometry (LC/MS-MS) for PFASs detection. This means that only the specific PFAS species of interest are detected; any other PFASs are overlooked.

The International Organization for Standardization (ISO) method ISO 25101:2009 specifies a method for detection and quantification of two PFASs species: PFOA and PFOS. PFASs are extracted and concentrated with solid phase extraction using commercially available copolymer cartridges, then separated with HPLC. Detection is via MS/MS. The standard is designed to work with unfiltered samples of drinking water, ground water, and surface water (fresh water and sea water).

US EPA method 537.1, updated in November 2018, quantifies up to 18 PFAS analytes including PFOS, PFOA, and PFHxS via LC-MS/MS and is designed for drinking water samples. The recent update increased the number of PFAS analytes from 14 to 18, adding GenX (hexafluoropropylene oxide dimer acid, HFPO-

DA) (ChemWatch, 2018). PFASs are extracted and concentrated with solid phase extraction using commercially available copolymer cartridges, then separated with HPLC and detected with MS/MS.

Some laboratories offer a modified US EPA Method 537 for other media, such as soils or ambient water (US EPA 2018). These modifications are not approved by the US EPA and have not undergone the same rigor as a standard US EPA test method. There are no standard EPA methods for analyzing PFASs in surface water, non-potable groundwater, wastewater, or solids, though US EPA is further developing methods for PFAS detection and quantification (US EPA, 2018).

ASTM offers two methods, D7979 for non-drinking-water aqueous samples and D7968 for soil/biosolid samples. Both methods us LC-MS/MS to separate, identify, and quantify PFAS analytes.

ASTM D7979-17 (ASTM, 2017). For non-drinking-water aqueous samples. Detection is via LC-MS/MS. Reporting ranges are listed on the website here https://www.astm.org/Standards/D7979.htm .
ASTM D7968. For soil/biosolid samples detection is via LC-MS/MS.

Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy
Multiple groups have used Particle-Induced Gamma ray Emission (PIGE) spectroscopy to measure total fluorine as a proxy for PFASs (CEH, 2018; Lang, 2016; Safer Chemicals Healthy Families 2018; Schaider, et al., 2017). PIGE is a rapid and inexpensive method to measure total fluorine in solid-phase samples that has been validated with LC-MS/MS methods (Ritter, et al., 2017). A negative result is indicative that no PFASs are present at or above the detection limit, as all PFASs contain fluorine. Positive results indicate that PFASs or other fluorine-containing molecules are present. In Schaider (2017), the LOD was ~16 nmol F/cm^2, and the LOQ was ~50 nmol F/cm^2.

Both the CEH (2018) and the Safer Chemicals Healthy Families and Toxic Free Futures partnership (SCHF/TFF, 2018) used PIGE to screen food packaging materials for fluorine. In both works, they divided results into three classes:

- No detectable fluorine- both surfaces register total fluorine counts per microcoulomb of beam of less than ~150 (CEH) or 125 (SCHF/TFF)
- Low fluorine content - at least one surface registers total fluorine counts per microcoulomb of beam of greater than ~150 and less than ~500 (CEH) or greater than 125 and less than 450 (SCHF/TFF); fluorine must be statistically significant at 3x above background
- High fluorine content - at least one surface registers total fluorine counts per microcoulomb of beam of greater than ~500 (CEH) or 450 (SCHF/TFF); fluorine must be statistically significant at 3x above background

High fluorine content had statistically significantly higher (on average 10x higher, CEH, or 5x higher, SCHF/TFF) levels of fluorine than those identified as low fluorine. Low fluorine content could have resulted from clay containing naturally-occurring fluorine, or from low levels of contamination in the product manufacturing process.

In the CEH (2018) work, there was only a single instance out of 137 products assessed with a suspected false PFAS positive fluorine result due to the bulk material used; it was not expected for PFASs to be needed for PLA plastics. The manufacturing process for this product, a black rigid PLA plate, used a fluorinated chemical as a “mold release agent”. The company has indicated that they have requested a non-fluorinated substitute for this use. However, this mold release agent was most likely a PFAS or a mix of PFASs as PFASs are known to be used for this function (Kissa, 2001). It is not truly a false positive if PIGE detects both unintentionally present PFASs and intentionally added PFASs; in both cases it is detecting PFASs present in the final product. It is possible that some of the other high fluorine results from the CEH (2018) work or SCHF/TFF (2018) work is the result of non-PFAS fluorinated chemicals, but a selection of results was validated with LC-MS/MS, and this did not reveal high fluorine PFASs-free samples.

Combustion Ion Chromatography (CIC)

Combustion ion chromatography (CIC) measures both total fluorine and organic fluorine. In this method, the sample is extracted, the sample is combusted at high temperatures (e.g. >900°C) to break down organic molecules, and the resulting ions are analyzed using an ion chromatograph. Different sample extraction methods select for organic, inorganic, or total fluorine. Additional experiments are necessary to distinguish which organofluorine molecules are present; CIC alone does not distinguish between different PFASs or even confirm that the organofluorine is in PFASs. This approach was initially described by Miyake et al. (2007) with a LOD of 1 ng F/L with water samples and 1 ug F/L with blood samples. In Wagner et al. (2013), the limit of quantification (LOQ) was 0.3ug/L with wastewater samples when extraction was performed by the adsorption of organofluorine chemicals on a synthetic polystyrene-divinylbenzene based activated carbon. CIC was used by CEH (2018) to validate results obtained using PIGE.

Total Oxidizable Precursor (TOP) Assay

In this method, fluorotelomer precursors are oxidized using persulfate in the presence of base to produce perfluorinated alkyl acids (PFAAs), such as PFOA and PFHxA; this technique only applies to precursors with an oxidizable CH2 carbon (Houtz & Sedlak, 2012). The PFAAs are then quantified using targeted LC-MS/MS. Total precursors are calculated based on the increase in PFAAs present in the initial sample compared to those present in the derivatized sample. Due to the derivatization step, the precise identity of the fluorotelomer precursors is unknown using this method. Any PFAS species not looked for, or without an oxidizable CH2 carbon that results in a PFAS species looked for, is not detected with this method.

Fluorescence-based Methods

Other than mass spectrometry, one of the most sensitive detection options is fluorometric (Trojanowicz & Koc, 2013). In this method, PFASs are derivatized with a fluorophore, separated, and detected fluorometrically (Ohya, Kudo, Suzuki, & Kawashima, 1998; Poboży, Król, Wójcik, Wachowicz, & Trojanowicz, 2011). Paired with HPLC for separation, the LOD for this method is 43 to 75 ng PFASs/L (Poboży et al., 2011). These requires derivatizable PFASs, and does not identify specific species.

Nuclear Magnetic Resonance (NMR) Spectroscopy

19F nuclear magnetic resonance (NMR) spectroscopy can detect total fluorine in a sample. This technique was used by Moody, Kwan, Martin, Muir, & Mabury (2001) in conjunction with LC-MS/MS to identify and quantify PFASs in aqueous environmental samples following a spill of 22,000 liters of PFASs-containing fire-fighting foam at L.B. Pearson International Airport in Toronto, ON (Moody et al., 2001). The LOD was 10 ug/L for a 100 mL sample.

X-ray photoelectron spectroscopy (XPS)

XPS detects total fluorine on the surface (0.01 µm) of a product, and has been applied to both textiles and food contact materials (Tokranov, 2019). This is the region that is directly in contact with food or skin. PIGE also detects surface fluorine, but at a much greater depth (100 - 250 µm). A high resolution XPS scan provides unique peaks for CF2 and CF3 groups, confirming the presence of organofluorine. The LOD was ~1.6 wt% F, assuming the rest of the material is carbon.

Mass spectrometry (MS) Methods

Mass spectrometry (MS) can be used to detect and quantify specific PFAS species. It is limited to detecting known PFAS species, and requires a standard for quantification. The matrix can interfere with ionization of the PFAS analytes, either suppressing or enhancing it, which can cause difficulties when detecting and quantifying PFASs in diverse samples (Martin et al., 2004). Isotopic standards, if available, can address this issue, though may result in decreased sensitivity (Martin et al., 2004). Specific interference effects have been described for phospholipids and fatty materials (Valsecchi et al., 2013). The use of tandem mass spectrometry, or MS/MS, allows for by high sensitivity and selectivity of specific PFAS species.

MS is typically preceded by a separation step. HPLC is suitable for most PFASs, though gas chromatography (GC) is more suitable for volatile species (Martin et al., 2004). Gas chromatography requires derivatizing ionic PFASs to convert them to volatile species, while neutral species can be directly analyzed due to their semi-volatile nature (Kempistry et al., 2018). Liquid chromatography is generally preferred over GC when possible because the derivatization step required for GC is time consuming and a source of uncertainty (Valsecchi et al., 2013).

One downside of MS techniques is that limited specific species of PFASs are analyzed. The choice of extraction, liquid chromatography, and mass spectrometry conditions defines which species are resolved, identified, and quantified in MS; not all PFAS species are quantified simultaneously. Certain species, such as fluorotelomer alcohols, are volatile and form adducts with LC modifiers, meaning that there are additional challenges to the measurement of this subclass of PFASs using LC/MS (Schaider, et al., 2017). As these species are commonly detected in food contact materials (Yuan, Peng, Huang, & Hu, 2016), it is important to ensure that fluorotelomer alcohols are included among the species accurately quantified by the test method.

Another downside of LC/MS is that it requires destruction of the sample. However, only a small sample is required, and this is not a barrier to its use with disposable food packaging materials.

Appendix B: Standards for Environmental Biodegradation and Composting

Multiple standards bodies have developed relevant standards for PFASs and food packaging around composting:

- ASTM
- CEN
- ABA
- ISO

The relevant ASTM compostability standards is D6400, Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities (ASTM, 2012). It does not consider PFASs.

ASTM D6400 has three requirements for compostability, none of which consider PFASs directly (ASTM, 2012):

- Disintegration during composting: Product must disintegrate such that remaining product fragments are not readily distinguishable from the other organic materials in the compost. Up to 10% of the product by weight can remain intact on a 2.0 mm sieve.
- Biodegradation: Specified tests (ASTM D5338, ISO 14855-1, or ISO14855-2) must demonstrate biodegradation, defined as conversion of ninety percent of organic carbon to carbon dioxide by the end of the test period.
- No adverse impacts on ability of compost to support plant growth: Compost generated with the product does not adversely impact the ability of the compost to support plant growth, relative to compost generated without the product; certain chemicals are red-listed. Concentration of regulated metals must be less than 50% of those prescribed for sludges or composts; in the US, regulated metals include arsenic, cadmium, copper, lead, mercury, nickel, selenium, and zinc (Table 3 of 40 CFR Part 503.13). Following OECD Guideline 208, the germination rate and the plant biomass of the sample composts must be no less than 90% for two different plant species.

The European Committee for Standardization (CEN) offers EN 13432, a harmonized European standard for industrial compostability that is similar to ASTM D6400. It requires:

- Disintegration: At least 90% of product must disintegrate to fit through a 2x2mm mesh.
- Biodegradation: Conversion of at least 90% of the material into CO2, water, and minerals following ISO 14855 (controlled aerobic composting), ISO 14851 (aerobic in water, oxygen demand), or ISO 14852 (aerobic in water, evolved CO2)
- Quality of the final compost and ecotoxicity: Compost generated with the product does not adversely impact the ability of the compost to support plant growth, relative to compost generated without the product. Following OECD Guideline 208, the germination rate and the plant biomass of the sample composts must be no less than 90%. Further, the composted material must not have an adverse effect on the bulk density, pH, salinity, volatile solids, total nitrogen, total phosphorus, total magnesium, total potassium, and ammonium nitrogen

characteristics of the compost (according to http://www.bpf.co.uk/topics/standards_for_compostability.aspx).
- Chemical analysis: Low levels of certain chemicals, mostly heavy metals: zinc, copper, nickel, cadmium, lead, mercury, chromium, molybdenum, selenium, arsenic, and fluoride. Fluoride is limited to 100 mg/kg dry sample (100 ppm) (http://www.bpf.co.uk/topics/standards_for_compostability.aspx).

While it does not explicitly consider PFASs, the fluorine limit of 100 ppm is sufficient to exclude intentionally added PFASs for water/grease resistance.

Standards Australia offers AS4736 for industrial composting and AS5810 for home composting. AS4736 was based on EN 13432 and AS5810 was based on the OK compost HOME label offered by Vinçotte (currently offered by TÜV AUSTRIA). AS4736 has requirements in the same four areas as EN 13432 with the same or very similar specifications; the primary divergence is the addition of a worm ecotoxicity test. Both use the 100 ppm limit on fluorine from EN 13432, which excludes PFASs.

The International Organization for Standardization (ISO) offers ISO 17088, specifications for compostable plastics. Similar to ASTM D6400 and EN 13432, ISO 17088 requires 90% biodegradation and disintegration (limited by a 2mm sieve), and OECD 208 for the quality of the resulting compost. ISO 17088 is aligned with ASTM D6400 with regards to chemical analysis and relies on the country-of-sale’s regulations for metals; this means that ISO 17088 would permit PFASs like ASTM D6400.

Appendix C: Certification Programs for Environmental Biodegradation and Composting

Multiple organizations certify products as compostable in industrial or home composting or environmentally biodegradable. Here, we summarize the following certifications:

- Biodegradable Products Institute (BPI) certified compostable
- Cedar Grove Accepted
- TÜV AUSTRIA (formerly run by AIB Vinçotte International) - OK Compost INDUSTRIAL, OK Compost HOME
    - OK compost INDUSTRIAL
    - Seedling label
    - OK compost HOME
    - OK biodegradable SOIL
    - OK biodegradable WATER
    - OK biodegradable MARINE
- DIN CERTCO
- Japan Bioplastics Association GreenPla

Biodegradable Products Institute (BPI) certifies products as compostable in industrial facilities based on ASTM D6400 and D6868. Currently, PFASs are allowed in products labeled and sold with this compostability certification. However, in a November 2017 statement, BPI declared that they are adopting the 100 ppm fluorine limit from EN 13432 for all future certifications and requiring a declaration that no fluorinated chemicals have been intentionally added (BPI, 2017). By December 31, 2019, companies must confirm that any inventory with fluorine above 100 ppm will no longer be labeled or marketed as BPI certified compostable (BPI, 2018).

Cedar Grove maintains a list of compostable products, including food packaging, based on ASTM D6400 and D6868 and further requiring a field test of compostability. Currently, PFASs are allowed in products labeled and sold with this certification. Cedar Grove has recently updated their standard to match BPI, adopting a 100 ppm fluorine limit that goes into effect on January 1, 2020 (Cedar Grove, 2019). However, unlike BPI, they have no explicit requirement that existing inventory must also be compliant by that date. Starting January 1, 2019, Cedar Grove requires an addendum to any submissions that asks for information such as fluorine content (> or < 100 ppm), the range of fluorine found, laboratory methods used, future R&D work that may involve fluorine or fluorine alternatives, and whether those alternatives are being assessed for hazard (Cedar Grove, 2019).

TÜV AUSTRIA offers certification of biodegradability (soil, water, marine) and compostability (home and industrial). In order to achieve the OK compost INDUSTRIAL label, the product must pass EN 13432, and comply with EU Packaging Directive (94/62/EEC); OK compost HOME uses similar methodology but modifies EN 13432 to mimic the lower temperature conditions in a home compost pile (http://www.tuv-at.be/certifications/ok-compost-industrial-ok-compost-home/). Due to the use of EN 13432 and its 100 ppm limit on fluorine content, OK compost INDUSTRIAL prohibits PFASs.

TÜV AUSTRIA offers certification for biodegradability in soil, water, and marine environments. Each has individual requirements for biodegradation, disintegration, and environmental safety/ecotoxicity, and chemical analysis. Effort is made to ensure that the resulting labels do not promote littering. All three certifications reference EN 13432 for the chemical analysis; this means the 100 ppm limit on fluorine applies to these certifications as well, and all three certifications would prohibit PFASs as a result.

DIN CERTCO and TÜV AUSTRIA both offer the Seedling Logo, which is also based on EN13432. As with OK compost INDUSTRIAL, due to the use of EN 13432 and its 100 ppm limit on fluorine content, the Seedling Logo excludes PFASs. The requirements are very similar to the OK compost INDUSTRIAL requirements. In addition to the Seedling Logo, DIN CERTCO also offers the DIN-Geprüft test mark for industrial compostability following EN 13432, which excludes PFASs, and biodegradability in soil following EN 17033 for biodegradable mulch films.

The Seedling Logo is also offered by the Australasian Bioplastics Association (ABA), following Australian Standard (AS) 4736, Biodegradable plastics - biodegradable plastics suitable for composting and other microbial treatment. AS4736 is based on EN 13432 with the additional requirement of a worm test, and does include the 100 ppm limit on fluorine, and thus, PFASs. ABA also offers the Home Compostable Verification logo, based on AS5810, which also includes the 100 ppm limit on fluorine and thus PFASs.

Japan Bioplastics Association certifies plastics as biodegradable under GreenPla using its own scheme that is similar to EN 13432 and ASTM D6400:

- Disintegration: Resulting compost must filter through a 2mM sieve
- Biodegradation: Test must follow ISO 16929 or ASTM D5338 (following restrictions from ASTM D6400)
- Compost quality/ecotoxicity: OECD 208 or following “Plant Tests Using Komatsuna (Brassica rapa var. pervidis)” prescribed in General Administrative Agency Bulletin No.5005 (Silkworm Farming)

As noted previously, while PFASs content and toxicity could be sufficient to result in a fail of OECD 208, the results from the recent CEH (2018) study reveal that at least some PFASs-containing food packaging can pass OECD 208. It is expected that PFASs-containing food packaging could pass this certification.

Loopholes and Barriers

Several loopholes and barriers allow for materials containing highly fluorinated chemicals. Two requirements in standards and certifications could address the presence of PFASs in food packaging products: The compost quality/ecotoxicity test OECD 208 and the chemical analysis requirements that include fluorine. However, only the chemical analysis requirements actually exclude PFASs.

OECD 208 is a ubiquitous test method in these schemes. OECD Guideline 208 is the Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test (OECD, 2006). Seeds are plants in control compost and compost containing the product. Seeds are evaluated 14-21 days after 50% emergence of seedlings in the control compost. Assessment endpoints include:

- Visual assessment of seedling emergence
- Dry or fresh shoot weight or height
- Visible detrimental effects on parts of the plant

While it is possible that this would disqualify some products due to PFAS toxicity, it is known that many products containing PFASs have passed this test (CEH, 2018). The guideline requires that the compost is at least 10% product. PFAS concentrations in food packaging is relatively low. Regulations limit fluorochemical concentration, typically allowed to range from 0.2 to 1.5%, though industrial technical application papers mention concentration ranges from 0.1-4% (Trier et al., 2017). We identified one study that followed OECD 208 to test toxicity of seven different PFASs, using Lactuca sativa (lettuce) and the endpoint of root elongation. In this study, the NOECs ranged from 0.1 - 3 mm and EC50s ranged from 0.142 - 4.186 mm Given a compost density of ~400 g/L (and knowing that compost density can range significantly), the final concentration of PFASs in PFASs/food packaging compost would be in the single digit mm range, which falls within the EC50 for root elongation, leading to an expectation that PFASs-containing food packaging would be revealed using OECD 208.

However:

- Not all PFASs share the same toxicity. The PFASs used in food packaging may be less toxic to plants than the PFASs used in this study.
- Not all plants respond to PFASs in the same manner. The plants used in the OECD 208 tests for compost certification may not have used lettuce, which was used in this study, or may have used a different endpoint.
- Synergistic or antagonistic effects from PFAS mixtures and other chemicals present.

Given the results from the CEH (2018), it seems likely that OECD 208 is not sufficient for excluding PFASs from compost.

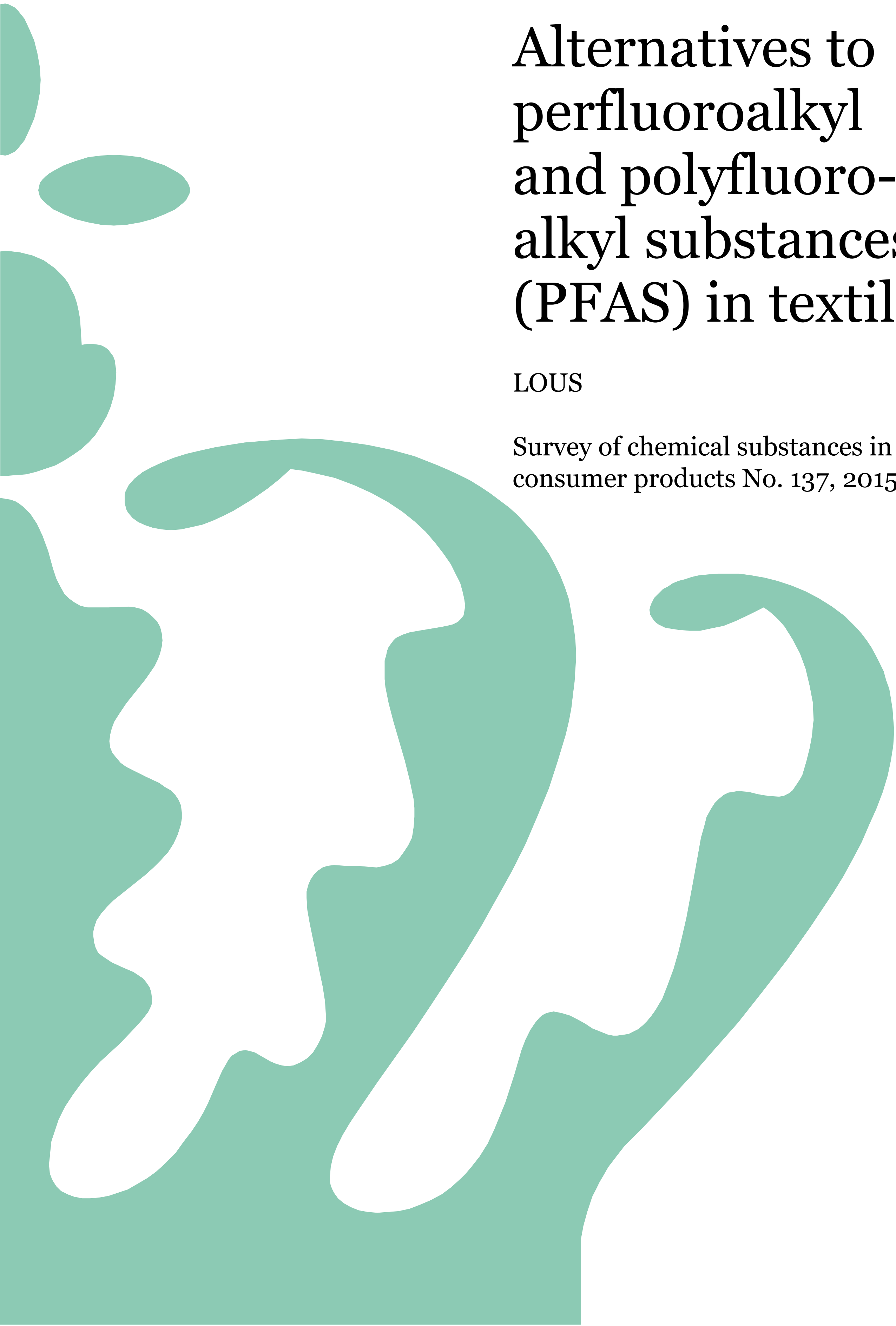
None of the chemical analysis requirements explicitly exclude PFASs. However, all of the standards and certifications based on EN 13432 include a 100 ppm limit on fluorine content. This corresponds to 0.01% of the food packaging. As mentioned above in the discussion on OECD 208, PFAS concentrations in food packaging may be 0.1% - 4% (Trier et al., 2017). Converting the percent PFASs to percent fluorine requires knowing the identity of the PFAS in question; 0.1% PFOA equates to almost 690 ppm fluorine, while PFOS corresponds to 650 ppm. As the size of the non-fluoro group increases, the corresponding ppm fluorine decreases. As the length of the perfluoro moiety increases, the corresponding ppm fluorine decreases. While a PFAS with a very large non-fluoro group could be present at 0.1% with fluorine levels below 100 ppm, the fluoro group is the functional group, and it would be expected that this particular PFAS requires a higher percentage to achieve the same water/grease-proofing. As a result, the 100 ppm fluorine limit is sufficient to exclude PFASs intentionally added for water/grease-proofing.

Danish Ministry of the Environment
Environmental Protection Agency

Alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in textiles

LOUS

Survey of chemical substances in consumer products No. 137, 2015



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Alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in textiles

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Foreword

A survey of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and other perfluoroalkyl and polyfluoroalkyl substances were undertaken in 2012 as part of the Danish Environmental Protection Agency's (EPA) surveys of the 40 substances/substance groups on the Agency's List of Undesirable Substances (LOUS). On the basis of the survey, the Danish EPA developed three strategy papers addressing (Danish EPA, 2013):

- risk management of PFOS and PFOS substances;
- risk management of PFOA and PFOA substances; and
- risk management of other perfluorinated substances.

Here, the substances are collectively referred to as PFAS.

The strategy papers note that there is a general lack of published data on the properties of the alternatives to the PFAS of most concern, partly because the data usually are protected by trade secrets, and partly because most of the scientific research has focused on a few polyfluorinated substances such as PFOS and PFOA, historically the substances of most concern.

In order to obtain further information on alternatives to the PFAS of most concern and to PFAS in general, the Danish EPA has launched two reviews:

- This study on non-fluorinated alternatives to PFAS-based impregnations agents for textiles, and
- a review of environmental and health properties of short-chain PFAS.

The objective of this study is:

- To identify non-fluorinated alternatives available for surface treatment and impregnation of textiles including waterproofing spray for private use. The alternatives may include other chemicals and technical non-chemical solutions;
- To provide environmental and health assessments for chemical alternatives.

Concurrently, under the Danish EPA's programme for surveys of chemical substances in consumer products, a survey of PFAS in textiles for children, including environmental and risk assessments of the releases of PFAS from the textiles, is being carried out.

The results of the projects contribute to the Danish EPA's considerations regarding the need for and feasibility of further regulation of the group of PFAS substances.

The project has been followed by a steering group consisting of:

- Louise Grave-Larsen, Danish Environmental Protection Agency
- Carsten Lassen and Marlies Warming, COWI
- Allan Astrup Jensen, NIPSECT.

Conclusion and summary

Objectives
The objectives of this study are to identify non-fluorinated alternatives available for surface treatment and impregnation of textiles and to provide environmental and health assessments for the chemical alternatives.

Performance criteria
Impregnation agents based on polyfluoroalkyl substances (PFAS) are widely used in textiles in order to achieve water, oil and dirt repellency of the fabric, while at the same time maintaining breathability. Besides repellency to water, oil and dirt, the PFAS-based impregnation agents provide repellency to alcohol and a high level of washing and dry cleaning durability.

Technical properties of marketed alternatives
Many manufacturers of impregnating agents have developed non-fluorinated alternatives to PFAS-based finishing agents in recent years in response to a demand for more "environmentally-friendly" finishing agents. Many different agents providing water repellency are marketed, but none of these agents provides efficient repellency against oil, alcohol and oil-based dirt. The alternatives may be used for both clothing and technical textiles, and agents appear to be available for all types of fibres and fibre blends.

Water repellent finishing agents based on paraffin and silicone chemistries have been available on the market for many years, and have been used for those applications where repellency against oil, alcohol and oil-based dirt have not been required.

Water repellent dendrimer-based impregnation agents are a relatively new group of repellents on the market. According to a new Danish survey of PFAS in children's clothing, many of the manufacturers of children's clothing have changed from PFAS technology to non-fluorinated dendrimer technology in recent years.

Alternatives based on polymer coatings (e.g. PVC or PUR) may provide repellency against water, oil and dirt, but the fabrics are not breathable, and have not been assessed further.

In summary, it can be concluded that no alternatives matching the PFAS-based repellents on all technical parameters are available. For some applications, where repellency against oil, alcohol and oil-based dirt is not required, the alternatives are considered to provide acceptable properties at costs at the same level as the costs of using the PFAS-based agents.

Paraffin repellents
Health assessment - The products in this group are liquid emulsions that, according to the producers, should not to be classified as hazardous to health. However, some of the known ingredients seem to be harmful. The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which is harmless in its pure form. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.

Environmental assessment - The products in this group are liquid emulsions that, according to the producers, should not to be classified as hazardous for the environment. Most components are readily biodegradable, are not bioconcentrated or accumulated in organisms and food chains, and the toxicity to aquatic and terrestrial organisms is insignificant even at concentrations above the water solubility.

Silicone repellents

Health assessment - The silicones most used in textile impregnation agents are based on polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH; they are inert and generally have no adverse effects. Various other siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, are intermediates for synthesis of silicone polymers used for textile impregnation. The siloxanes are volatile and most exposures will occur by inhalation. Specifically D4 is suspected of damaging fertility, and D5 is a potential carcinogen. The commercial emulsions often contain other substances such as isotridecylalcohol, which is registered under REACH and is more harmful than the siloxanes. Some commercial products contain substances that are powerful irritants.

Environmental assessment - Siloxanes are persistent and are widespread in the environment but are found mostly in urban areas and in the aquatic environment. High levels have been found in livers of fish caught close to outlets of sewage treatment plants. The siloxanes are removed from the aqueous phase by sedimentation, and have a long half-life in sediments. In soils, depending on the conditions, siloxanes are transformed into hydroxylated forms, which may still be persistent.

The bioconcentration factors and bioaccumulation factors for D4 are high, indicating D4 may have a high potential to accumulate in aquatic organisms. According to an ECHA expert group, D4 met the criteria for a PBT and a vPvB substance[1]. D5 also met the criteria for a vPvB substance due to its persistence in sediments and a high bioconcentration factor in fish. D6, MM, MDM, MD2M, and MD3M were not considered PBT or vPvB substances by the notifiers under REACH, but the substances have not yet been evaluated by ECHA. PDMS has not been evaluated for lack of data.

The commercial products also contained substances other than siloxanes; some known, some unknown. Isotridecyl alcohol is less persistent but more toxic to aquatic organisms. A quaternary ammonium compound used was classified as harmful for the environment.

Dendrimer-based repellents

Health assessment - There are no data on health properties of the active substances and other components, but the producers of commercial products have included a few health data in the MSDSs and made some proposals for classification of the product. According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently for an assessment, but some of the products contain unknown siloxanes (likely among those discussed above), cationic polymers, isocyanates or powerful irritating organic acids. In general, the health assessment information for this group of chemicals is insufficient for an assessment of the possible health effects of the impregnation agents.

Environmental assessment - The product compositions of these repellents were not specified sufficiently for an environmental assessment, but some of the products contain unknown siloxanes, cationic polymers, isocyanates or powerful irritating organic acids. According to the producer's information, these products should not be labelled or classified as harmful for the environment, but on the basis of the available information, it is not possible to evaluate these statements.

Polyurethane repellents

Health assessment - Only one commercial product is identified. Its composition is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should

---

[1] PBT: persistent, bioaccumulative and toxic. vPvB: very persistent and very bioaccumulative

not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS. Generally, the content of organic isocyanates makes products potentially hazardous to skin and mucous membranes. Therefore, it is not possible to assess the possible health effects of the agents in detail.

Environmental assessment - The composition of the commercial product is not detailed, either qualitatively or quantitatively. According to the producer's information, the products should not be labelled or classified as harmful for the environment. However, it is not possible to verify these claims because of lack of relevant data.

Other repellents

Health assessment - For one commercial product, described as a non-ionic polymer, ester and hydrocarbon compound, it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients". However, no documentation for this was provided, and some risk phrases were mentioned for the product indicating skin- and eye irritating properties and harmfulness if swallowed. Therefore, it was not possible to verify the producers' claim that it is non-hazardous product.

For a cationic pyridine derivative and a nanomaterial based repellent, the health data were insufficient for an assessment.

Environmental assessment - For one commercial product, described as a non-ionic polymer, ester and hydrocarbon compound, it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients. However, no documentation for that claim regarding effects on the environment was given.

For a cationic pyridine derivative repellent, the environmental data were insufficient for an assessment.

Summary regarding persistence

One of the main concerns regarding the PFAS-based impregnating agents is the formation and release of persistent PFAS or precursors for persistent PFAS. Some uncertainty exists as to the potential release of persistent siloxanes during the lifecycle of silicone-based repellents. For the other alternatives, the available data do not indicate the potential for any significant releases of persistent substances.

Main data gaps

For most of the alternative impregnation agents reviewed, there is insufficient qualitative and quantitative public information about the ingredients. Most products do not have information available because they are protected by trade secrets. Only a few specific ingredients are declared, and for these, only limited data on health and environmental properties are available. For some siloxanes used as intermediates in production of silicon polymers, much information on health and environmental properties of the substances exists, but it is unclear to what degree these siloxanes are ingredients or impurities in the commercial products.

For all of the alternatives, hardly any information on trace levels of raw materials, intermediates and degradation products in the final textile products is available. Furthermore, no data on the possible formation of hazardous degradation products by waste disposal of the textiles are available. However, based on the available knowledge about chemical structures, persistence, bioaccumulation and toxicities of the assessed alternatives, the conclusion is that most of the alternatives (apart from those that are silicone-based) possibly do not contain or generate persistent substances at significant levels and are therefore preferable to the persistent PFAS-based impregnation agents from an environmental perspective.

Konklusion og sammenfatning

Formål
Formålet med denne undersøgelse er at identificere ikke-fluorerede alternativer til overfladebehandling og imprægnering af tekstiler og udarbejde miljø- og sundhedsmæssige vurderinger for de kemiske alternativer.

Funktionskrav
Imprægneringshandlingsmidler baseret på polyfluoralkyl stoffer (PFAS) er almindeligt anvendt i tekstiler for at give disse vand-, olie- og smudsafvisende egenskaber, mens stoffets åndbarhed samtidig bevares. Udover at gøre tekstilerne afvisende over for vand, olie og snavs, gør de PFAS-baserede imprægneringmidler tekstilerne afvisende over for alkohol og midlerne har samtidig en god bestandighed ved vask og kemisk rensning.

Tekniske egenskaber af markedsførte alternativer
Mange producenter af imprægneringsmidler har i de senere år udviklet ikke-fluorerede alternativer til PFAS-baserede efterbehandlingsmidler som følge af en efterspørgsel efter mere "miljøvenlige" imprægneringsmidler. Der markedsføres mange forskellige midler, som kan gøre tekstilstoffer vandafvisende, men ingen af disse midler er effektive med hensyn til at gøre tekstilerne afvisende over for olie, alkohol og oliebaseret snavs. Alternativerne kan anvendes til både beklædning og tekniske tekstiler, og der synes at være midler tilgængelige for alle typer af fibre og fiberblandinger.

Vandafvisende efterbehandlingsmidler baseret på paraffin- og silikonekemi har været tilgængelige på markedet i mange år, og er blevet brugt til de anvendelser, hvor afvisende egenskaber i forhold til olie, alkohol og oliebaseret snavs ikke har været påkrævet.

Vandafvisende, dendrimer-baserede imprægneringsmidler er en relativt ny gruppe af imprægneringsmidler på markedet. Ifølge en ny dansk kortlægning af PFAS i børnetøj, har mange af producenterne af børnetøj i de seneste år skiftet fra PFAS teknologi til ikke-fluoreret dendrimer-teknologi.

Alternativer baseret på polymerbelægninger (f.eks. PVC eller PUR) kan gøre tekstiler afvisende over for vand, olie og snavs, men tekstilstofferne er ikke åndbare, og er ikke vurderet yderligere.

Sammenfattende kan det konkluderes, at der ikke findes alternativer, som matcher PFAS-baserede imprægneringsmidler på alle tekniske parametre. Til nogle anvendelser, hvor afvisende egenskaber i forhold til olie og oliebaseret snavs ikke er påkrævet, anses alternativerne for at give acceptable egenskaber. Omkostningerne ved brug af de alternative midler er på niveau med omkostningerne ved anvendelse af de PFAS-baserede midler.

Paraffin-baserede imprægneringsmidler
Sundhedsvurdering - Produkterne i denne gruppe er flydende emulsioner, der ifølge producenterne, ikke skal klassificeres som sundhedsfarlige. Men nogle af de kendte bestanddele synes at være skadelige. Den vigtigste bestanddel i de fleste produkter er paraffinolie/voks, dvs. blandinger af langkædede alkaner (lineære alifatiske kulbrinter), der er harmløse i sin rene form. Produkternes sammensætningerer primært fortrolige, men det vides at nogle produkter også indeholder isocyanater, dipropylenglycol, metalsalte eller andre uspecificerede stoffer, som kan være skadelige.

Miljøvurdering - Produkterne i denne gruppe skal ifølge producenterne, ikke klassificeres som farlige for miljøet. De fleste er let bionedbrydelige, biokoncentreres ikke og ophobes ikke i organismer eller fødekæder, og toksiciteten over for vand- og jordorganismer er ubetydelig, selv ved koncentrationer over vandopløseligheden.

Silikone-baserede imprægneringsmidler

Sundhedsvurdering - De silikoner, som mest anvendes i imprægneringsmidler til tekstiler, er baseret på polydimethylsiloxaner (PDMS). Disse siloxaner er registreret i REACH, de er inerte og har generelt som polymere ingen skadelige effekter. Forskellige andre siloxaner, især de cykliske siloxaner kendt som D4, D5 og D6 og de lineære siloxaner HMDSO, MDM, MD2M og MD3M, er mellemprodukter ved syntese af de silikone-polymere, der anvendes til tekstilimprægnering. Siloxanerne er flygtige, og de største eksponeringer vil forekomme ved indånding. Specifikt D4 er mistænkt for at skade forplantningsevnen, og D5 har potentielt kræftfremkaldende egenskaber. De kommercielle emulsioner indeholder ofte andre stoffer, såsom isotridecylalcohol, som er registreret i REACH, og er mere skadelig end siloxanerne. Nogle kommercielle produkter indeholder stoffer, som er stærkt irriterende.

Miljøvurdering - Siloxaner er persistente og er udbredt i miljøet, men findes primært i byområder og i vandmiljøet. Høje niveauer er fundet i lever af fisk, fanget tæt på udløb fra renseanlæg. Siloxanerne fjernes fra vandfasen ved sedimentation, og har en lang halveringstid i sedimenter. I jord bliver siloxaner, afhængigt af forholdene, omdannet til hydroxylerede metabolitter, som dog stadig kan være problematiske.

Biokoncentrerings- og bioakkumuleringsfaktorerne for D4 er høje, hvilket indikerer, at D4 kan have et stort potentiale for ophobning i vandlevende organismer. Ifølge en ECHA ekspertgruppe, opfylder D4 kriterierne for at være et PBT og vPvB stof[2]. D5 levede også op kriterierne for at være et vPvB-stof på grund af sin persistens i sedimenter og en høj biokoncentrationsfaktor i fisk. D6, MM, MDM, MD2M, og MD3M blev ikke betragtet som PBT eller vPvB stoffer af registranter under REACH, men stofferne er endnu ikke blevet evalueret af det Europæiske Kemikalieagentur, ECHA. PDMS er på grund af manglende data ikke blevet evalueret.

De kommercielle produkter indeholdt også andre stoffer end siloxaner - nogle kendte, andre ukendte. Isotridecyl alkohol er mindre persistent, men mere giftigt for vandlevende organismer. En kvaternær ammoniumforbindelse, som er anvendt, blev klassificeret som skadelig for miljøet.

Dendrimer-baserede imprægneringsmidler

Sundhedsvurdering - Der er ingen data om sundhedsmæssige egenskaber af de aktive stoffer og andre komponenter, men producenterne af kommercielle produkter har medtaget et par sundhedsdata i sikkerhedsdatabladene og givet nogle forslag til klassificering af produktet. Ifølge producentens oplysninger skal disse produkter ikke mærkes eller klassificeres som skadelige. Produkternes sammensætninger blev ikke angivet i tilstrækkelig grad til en vurdering, men nogle af produkterne indeholder ukendte siloxaner (sandsynligvis blandt de som er diskuteret ovenfor), kationiske polymere, isocyanater eller stærkt irriterende organiske syrer. Generelt er der utilstrækkelige sundhedsmæssige informationer for denne gruppe af kemikalier til, at der kan udarbejdes en sundhedsvurdering af imprægneringsmidlerne.

Miljøvurdering - Produktsammensætningen af disse imprægneringsmidler blev ikke angivet tilstrækkeligt detaljeret til, at der kan foretages en miljøvurdering, men nogle af produkterne indeholder ukendte siloxaner, kationiske polymerer, isocyanater eller kraftigt irriterende organiske syrer. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som

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[2] PBT: persistent, bioakkumulerende og toksisk. vPvB: meget persistent og meget bioakkumulerende.

skadelige for miljøet, men på grundlag af de foreliggende oplysninger, er det ikke muligt at vurdere dette.

Polyurethan-baserede imprægneringsmidler

Sundhedsvurdering - Der er kun fundet to kommercielle produkter. Deres sammensætninger er ikke beskrevet, hverken kvalitativt eller kvantitativt. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som sundhedsskadelige. Ikke desto mindre er der flere faresætninger for sundhedsfare nævnt i sikkerhedsdatabladet for et af produkterne. Generelt kan indholdet af organiske isocyanater gøre disse produkter potentielt farlige på hud og slimhinder. Det er derfor ikke muligt at vurdere de mulige sundhedsmæssige affekter af imprægneringsmidlerne i detaljer.

Miljøvurdering - Sammensætningen af de kommercielle produkter er ikke beskrevet, hverken kvalitativt eller kvantitativt. Ifølge producentens oplysninger, skal disse produkter ikke mærkes eller klassificeres som skadelige for miljøet. Det er imidlertid ikke muligt at verificere disse udsagn, da der mangler relevante data.

Andre imprægneringsmidler

Sundhedsvurdering - For et kommercielt produkt, der er beskrevet som en ikke-ionisk polymer, organisk ester og carbonhydrid, er det angivet af producenten at produktet ikke indeholder ”indberetningspligtige mængder af farlige stoffer". Der er dog ikke givet dokumentation for denne påstand vedrørende sundhedsmæssige effekter, og der er for produktet angivet nogle risikosætninger, som indikerer, at produktet er hud- og øjenirriterende og skadeligt ved indtagelse. Det var derfor ikke muligt at verificere producenternes angivelse af, at produktet er ufarligt.

For et kationisk pyridinderivat og et nano-baseret imprægneringsmiddel var de sundhedsmæssige data utilstrækkelige for en vurdering.

Miljøvurdering - For et kommercielt produkt, der er beskrevet som en ikke-ionisk polymer, ester og carbonhydrid, blev det angivet af produktet ikke indeholdt: "indberetningspligtige mængder af farlige stoffer". Der har ikke været nogen dokumentation for dette til rådighed.

For et kationisk pyridinderivat imprægneringsmiddel var de tilgængelige miljødata utilstrækkelige for en vurdering.

Sammenfatning vedrørende persistens

En af de største bekymringer vedrørende PFAS-baserede imprægneringsmidler er dannelse og udslip af persistente PFAS eller forstadier (precursers) til persistente PFAS. Der er nogen usikkerhed med hensyn til de potentielle udslip af persistente siloxaner i livsforløbet af silikone-baserede imprægneringsmidler. For de andre alternativer, indikerer de foreliggende data ikke noget potentiale for væsentlige udslip af persistente stoffer.

Vigtigste datamangler

For de fleste af de alternative imprægneringsmidler, som er gennemgået, er der ikke tilstrækkelig kvalitativ og kvantitativ, offentligt tilgængeligt information om bestanddelene. De fleste produkters sammensætning er forretningshemmeligheder. Kun nogle få specifikke bestanddele er angivet, og for disse er der kun begrænsede data om sundheds- og miljømæssige egenskaber tilgængelige. For nogle siloxaner, der anvendes som mellemprodukter i produktionen af silikone-polymere, findes der megen information om stofferne sundheds- og miljøegenskaber, men det er uklart, i hvilken grad disse siloxaner er til stede som tilsigtede bestanddele eller urenheder i de kommercielle produkter.

For alle alternativerne, er der næsten ingen oplysninger om rester på sporniveau af udgangsstoffer, mellemprodukter og nedbrydningsprodukter i de endelige tekstilprodukter. Desuden er der ingen data til rådighed om den mulige dannelse af farlige nedbrydningsprodukter ved bortskaffelse af tekstilerne som affald. Baseret på den tilgængelige viden om kemiske strukturer, persistens, bioakkumulering og toksicitet af de vurderede alternativer, kan det konkluderes, at de fleste af alternativerne (bortset fra de silikone-baserede) formentligt ikke indeholder eller genererer persistente stoffer i signifikante mængder, og som derfor ud fra et miljømæssigt perspektiv vil være at foretrække frem for de persistente PFAS-baserede imprægneringsmidler.

1. Introduction

1.1 Background

Finishing agents based on polyfluoroalkyl substances (PFAS) are widely used in textiles in order to achieve water, oil and dirt repellency of the material, while at the same time maintaining breathability. The use of PFAS in textile production accounts for about 50% of global use of PFAS.

PFAS-based agents for impregnation of textiles are polymers which consist of a non-fluorinated backbone with polyfluoroalkyl side chains, also designated side-chain-fluorinated polymers (Buck et al., 2011). The main polymers can be distinguished from one another by the linkage (acrylate and/or methacrylate, urethane, and oxetane) between the polymer backbone and the length of the polyfluoroalkyl side chains.

Until recently, the side-chains have mainly been based on 8:2 fluorotelomer alcohols, i.e. they consist of a chain of eight perfluorinated carbon atoms and two carbon atoms without fluorine (C_8 chemistries). PFAS extracted from textiles have varying chain lengths as demonstrated in many studies (e.g. Herzke et al., 2009; Knepper et al., 2014), and similarly, the side-chain-fluorinated polymers probably have fluoroalkyl side-chains of varying length. PFAS extracted from textiles with agents based on C_8 chemistry have been demonstrated to include significant amounts of substances with longer chain lengths. Due to increased attention to the harmful effects of C_8 substances on human health and the environment, the application of polymers with polyfluoroalkylated side chains based on short-chain fluorine chemistry (C_4-C_6 chemistry) has been growing in recent years. Several of the ongoing projects on substitution of the PFAS-based impregnation agents concern the feasibility of using agents based on short-chain fluorine chemistry.

The side chains of the PFAS-based polymers typically include a perfluorinated part. If released by degradation of the impregnating agents, the substances may subsequently be degraded to persistent perfluorinated compounds in the environment. The short-chain PFAS are as persistent in the environment as long-chain homologues, but do not bioaccumulate to the same extent as the long-chain substances, as they are excreted more rapidly from the organisms studied (as reviewed by Lassen et al., 2013).

Our knowledge of most PFAS is limited in terms of usage and possible environmental and health impacts. Therefore, more knowledge is required about PFAS, but also about other textile impregnation agents based on chemistries other than PFAS. In this project, the term “alternatives to PFAS” in textiles refers to textile impregnation agents being free of fluorine chemistry.

1.2 Contact to manufacturers and users of the products

During searching for alternative products and communication with the industry, the following manufacturers of fluorine-free water repellents have been contacted:

- Rudolph Group
- Organoclick
- Nicca
- Archroma
- Schoeller

- Crypton/Nanotex
- Huntsman
- 3M
- Freudenberg.

The companies were contacted by telephone and/or -e-mail and asked for product information on:

1) Application ranges of the alternative agents,
2) Technical advantages and disadvantages as compared to fluorocarbon-based agents,
3) Price of agents as compared to fluorocarbon-based agents,
4) Chemical composition of alternatives and the generated surface film, and
5) Data on the environmental and health properties of alternative agents and their constituents.

Some of the companies provided technical and material data sheets, whereas other companies considered such documents as confidential. Of the 11 companies contacted, nine have responded and provided information with varying levels of detail.

Some of the companies openly shared their product information. Most were less willing to share details on the chemical composition of their products. This clearly reflects that the market for non-fluorinated alternatives for textile impregnation is relatively young and under development, causing product developers to carefully protect their innovations. In some cases, a company might even refrain from patenting their solution because, globally, patents are not necessarily respected.

Apart from the suppliers of alternatives, the following organizations/companies have been contacted in order to identify the relevant manufacturers of alternatives as well as to gather more general information about the topic with a focus on Danish activities:

- Kvadrat (manufacturer of design textiles)
- IKEA (furniture manufacturer and retailer)
- Egetæpper (manufacturer of carpets)
- Ecco (manufacturer of shoes)
- Euratex (European trade association)
- TEGEWA (German trade association)
- Dansk Fashion and Textile (Danish trade association)
- SWEREA Group (Swedish Research Institute).

Limited information has been obtained from these market actors, as the companies consider information on suppliers to be confidential information.

1.3 Research activities and assessments of alternatives

In order to develop, test and assess alternatives to PFAS-based textile finishing technology, several research activities have been undertaken or are ongoing.

"Zero Discharge of Hazardous Chemicals (ZDHC)" - A research report on “Durable Water and Soil Repellent Chemistry in the Textile industry” has been published within the framework of the Roadmap to Zero Discharge of Hazardous Chemicals (ZDHC) concerted action. ZDHZ was formed in 2011, consisting of a group of major apparel and footwear brands and retailers helping lead the industry towards zero discharge of hazardous chemicals by 2020. The ZDHC brands have collaborated with the Outdoor Industry Association (OIA), the European Outdoor Group (EOG), Bundesverband der Deutschen Sportartikel-Industrie e.V. (BSI) (German Sporting Goods Association), and representatives from the chemical industry to understand opportunities, challenges and limitations for eliminating durable water repellent (DWR) technologies associated with long-chain

PFAS. The project included non-fluorinated DRW chemistries as well as short-chain fluorine chemistries.

SUPFES – In Sweden, an ongoing project called "Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources" (SUPFES), coordinated by Swerea IVF, aims to help industry find alternatives that can replace fluorinated chemicals in textiles. Within the project, a number of scientific and industrial partners collaborate to assess the risks of different PFAS-free finishing agents and ensure that the new alternatives really provide the desired functionality. Contact has been established with the project. The project started in the middle of 2013, and the project secretariat has informed the authors that initial project outputs are expected in 2015.

"Development of environmentally friendly impregnation agents for textiles" – The Danish Technological Institute is currently conducting a project to develop environmentally friendly impregnating agents for the textile industry, supported by the Danish EPA. The project runs for two years and builds on existing knowledge and known alternative products. The alternatives are examined to determine whether they can be improved or form a basis for the development of new repellent agents. So far, no agents beyond the marketed alternatives described in this survey have been developed or tested.

TEX-SHIELD project - The TEX-SHIELD project "Environmental friendly and durable oil and water repellent finish on technical textile" is a new project supported by funding from the European Union's seventh Framework Programme and started in January 2013. The overall project aim is to provide the European textile industry with an alternative material to C_8 PFAS chemistries whilst refining comparable performance. The project also includes finishing agents based on short-chained PFAS. The project has so far not published outputs, but some draft documents are available via the internet (TEX-SHIELD, 2013).

"Smart Textiles" - Within the Smart Textiles framework (cooperation between University of Borås, SP Technical Research Institute of Sweden, Swerea IVF and the Inkubator in Borås), a collaborative project between Smart Textiles and the manufacturer of finishing agent OrganoClick has been undertaken. In the project, a fluorocarbon-free, biodegradable and durable treatment has been tested in cooperation with major outdoor apparel brands such as Haglöfs, Norröna and Bergans (Smart Textiles, 2014). Contact has been established with the project coordinators. The agents from OrganoClick are further described in section 0 along with information obtained on environmental and health properties.

"Smart Finishing Agents" – The Danish Technological Institute, in cooperation with the Knowledge Centre for Intelligent Textiles, released the report "Smart finishing agents" as a result of the project "More functionality in everyday clothes". The aim of the report was to help apparel manufacturers who want to implement more functionality in their products. The project did not specifically focus on the identification of non-PFAS technologies. The finishing agents identified that can provide stain-resistant and stain removal properties all involved PFAS technologies.

UNEP assessment of alternatives to PFOS - Within the framework of the Stockholm Convention, alternatives to perfluorooctane sulfonate (PFOS) and its derivatives are currently reviewed by the Persistent Organic Pollutants (POPs) Review Committee. The review includes, among other applications, the use of PFOS and its derivatives in textiles. Although the PFAS-based repellents for textiles are not based on PFOS, the review includes information on some of the chemical groups considered alternatives for PFAS-based repellents. The chapters on human health and environmental assessments of alternatives make reference to the most recent draft version of the review (UNEP, 2013). A final version of the review is under preparation, but was not published when the editing of this report closed.

2. Overview of fluorine-free alternatives

2.1 Performance criteria and action of the PFAS-based repellents

Durable water and oil repellents are topical finishes applied to fabrics to provide protection against water, oil and soil. These finishes also extend the life of products and keep them looking newer longer (ZDHC, 2012).

The required performance level of the repellent finishes is dependent on their intended uses, the apparel products and other important factors such as their durability to laundering and dry-cleaning, resistance to abrasion and fabric breathability (ZDHC, 2012).

As described by ZDHC (2012), durable water repellent (DWR) finishes are mostly applied to fabrics after dyeing and/or printing, but before the fabrics are made into garments. The PFAS-based repellents are polymers with pendant fluoroalkyl chains attached to the polymer backbone. The side-chain fluorinated polymers are applied as a thin film on the fabric surface, usually in combination with other finishing auxiliaries, by a pad-dry-cure process (as reviewed by Knepper et al., 2014). In this process, the dry fabric is passed through a bath of the aqueous dispersion, and then squeezed under high pressure between pads to remove excess material, followed by drying and curing in an oven at temperatures up to 180°C. The term drying is used for the evaporation of the solvent, whereas curing is a synonym for the polymerization of the individual monomers. Curing is mandatory for cross-linking techniques (as reviewed by Knepper et al., 2014).

An optimized water and oil repellent finish is designed for a specific fabric based on its fibre type and fabric construction. The finish forms an array of microscopic polymer domains on the fabric surface (not a film or coating) with the fluorinated chains perpendicular to the fabric surface and close enough to one another to act like a continuous surface, thus preventing water and oils from reaching the fabric (ZDHC, 2012).

The requirements as to breathability exclude various polymer coatings used to waterproof textiles as possible alternatives. The polymer coatings based on e.g. PVC, PU or acryclic are used to waterproof some types of rainwear, tarpaulins, bags, etc. and may also provide some resistance to oil and dirt.

2.2 Overview of chemistry of alternatives on the market

According to a research report on “Durable Water and Soil Repellent Chemistry in the Textile industry” (ZDHC, 2012), it is possible to differentiate between five non-fluorinated water-repellent chemistries. The specific products typically contain smaller modifications to the general chemistries, e.g. through the presence of certain functional groups.

The five non-fluorinated chemistries mentioned in detail in the report are:

- Paraffin repellent chemistries;
- Stearic acid-melamine repellent chemistries;

- Silicone repellent chemistries;
- Dendrimer based repellent chemistries;
- Nano-material based repellent chemistries.

The report briefly mentions that the information on commercially available non-fluorinated chemistries made available by chemical manufacturers includes the acrylic- and urethane-based (PUR-based) chemistries, but the report does not describe these chemistries in detail.

The report reached the conclusion that there are a number of products on the market based on non-fluorinated chemistries, which provide durable water repellency, whereas non-fluorinated chemistries for oil and dirt repellency are limited (ZDHC, 2012).

A recent review of non-PFAS alternatives for water repellency and stain release from the apparel manufacturer Marks & Spencer (2014) provides a non-exhaustive list of products with an indication of repellent types and the fibres that can be treated (Table 1). The table indicates a broader range of products than indicated above.

The review (Marks & Spencer, 2014) also lists a few PFAS-free products offering stain release (see Table 1). For Arristan HPC, product details were not available on how stain repellency was achieved from the report or the suppliers' website. Technical data sheets of the Phobotex products disclose that the property applies only to water-based stains and not to oil-based stains.

TABLE 1
WATER REPELLENCY (INCLUDING WATER-BORNE STAINS) – EXAMPLES OF SUGGESTED PRODUCTS (MARKS & SPENCER, 2014)

Supplier	Product	Type	Fibres
Huntsman	Phobotex RHP Phobotex RSH Phobotex RHW Phobotex JVA	Fat modified resin	All
	Phobotex WS/BC	Silicone	Synthetics/blends
	Phobotex SSR* Phobotex HSR*	Hydrophilic copolymer	Synthetic and blends
Archroma	Arkophob FFR	Wax	All
CHT/Bezema	Zero F1	Paraffin dispersion	All
	Arristan HPC*	Hydrophilic copolymer	Synthetics
Devan	H2O Repel	Not known	Cotton, Polyester
LJ Specialities	Itoguard NFC	Fatty acid/paraffin	Cellulosic, Synthetics
	Itoguard NFC 90	Botanical extracts	Cellulosic, Synthetics
Rudolf	Ruco-dry ECO	Dendrimer	All
Sarex	Careguard FF	Not known	All
Schoeller	ecorepel	Paraffin	All
Texchem	Texfin HTF	Modified wax dispersion	All

Supplier	Product	Type	Fibres
Tanatex	Baygard WRC	‘3D’ Molecules	Cotton, blends
	Baygard WRS	‘3D’ Molecules	Synthetics, blends

* Products also offering stain release. Stain release is only available for synthetic fibres (Marks & Spencer, 2014).

2.3 Overall comparison between PFAS-technology and alternative technologies as provided by manufacturers

Several of the manufacturers produce repellents based both on PFAS and alternative technologies and provide an overall view of the differences in performance between the different technologies. The following tables provide comparisons as described by the manufacturers themselves.

According to Rudolf Group, which manufactures PFAS-based impregnating agents based on C_6 and C_8 chemistry as well as alternatives based on dendrimer technology (see section 5), the dendrimer-based agents have some drawbacks as they do not provide oil repellency (Table 2). The dendrimers technically have some advantages in providing soft textiles and excellent low-temperature curing. Prices are indicated as "very competitive".

TABLE 2
COMPARISON OF PERFORMANCE OF IMPREGNATING AGENTS SUPPLIED BY RUDOLF GROUP AS DESCRIBED BY THE COMPANY (RUDOLF GROUP, 2010)

Performance	C_8-chemistry	C_6-chemistry	Bionic-Finish ECO Dendrimer technology
Water repellency	Very good	Very good	Very good
Oil repellency	Good	Alike	No oil repellency
Washing durability	Very high	High	High
Dry cleaning	Good	Moderate	None
Low-temperature curing	Poor	Good	Excellent
Handle	Moderate	Slightly softer	Soft
Price	"Normal"	Higher	Very competitive

SIMILARLY ARCHROMA, WHICH PRODUCES AN ALTERNATIVE IMPREGNATING AGENT BASED ON ENCAPSULATION WAX TECHNOLOGY (SEE SECTION 3) AND VARIOUS PFAS-BASED AGENTS, INDICATES THAT THE NON-FLUORINATED ALTERNATIVES HAVE THE DRAWBACKS OF NOT PROVIDING OIL AND ALCOHOL REPELLENCY, AS WELL AS OIL AND WATER-BASED STAIN RELEASE (TABLE 3). ALL TYPES OF AGENTS PROVIDE WATER REPELLENCY.

TABLE 3
COMPARISON OF PERFORMANCE OF IMPREGNATING AGENTS AS DESCRIBED BY THE ARCHROMA (BASED ON ARCHROMA, 2014)

Performance	Water repellency	Oil repellency	Alcohol repellency	Stain release *	Abrasion resistance	Self cleaning
Fluorinated						
F-(Meth)Acrylates	+	+	+	+	+/-	-
F-Urethanes	+	+	+	+	+	-

Performance	Water repellency	Oil repellency	Alcohol repellency	Stain release *	Abrasion resistance	Self cleaning
F-Silicones	+	+	+	+	-	-
F-Particle	+	+	+	-	+	+
Non-fluorinated						
(Meth)Acrylates/ Urethanes	+	-	-	+/-	+/-	-
Silicones	+	-	-	-	-	-
Waxes	+	-	-	-	-	-
Dendrimers	+	-	-	-	+/-	-
Particle	+	-	-	-	+	+

* Oil and water-based stains.

These comparisons are in accordance with the general view that non-fluorinated alternatives do not provide oil and alcohol repellency, but otherwise largely are comparable with the fluorinated impregnation agents.

3. Paraffin repellent chemistries

3.1 Chemistry

Water repellent chemistry based on paraffin is one of the earliest technologies used. Paraffins/alkanes are long-chain hydrocarbons with the general molecular formula C_nH_{2n+2}.

The repellent products are typically emulsions of paraffins containing metal salts of fatty acids, usually stearic acid. The metals used most are aluminium, zinc and zirconium.

The metal ion, e.g. Zr^{2+}, provides fixation onto the fibre, and ensures that the water repellent groups have the right orientation on the fibre surfaces (Figure 1). The paraffin emulsions are generally compatible with other types of textile finishes, but show also increased flammability (ZDHC, 2012). Water repellency arises also from the ability of the metal ions to support the formation of macromolecules, which arrange as a fatty layer around the fibre (Lang, 2014, personal comm.).

Paraffinic repellents do not repel oil and are generally not (very) durable to laundering and dry cleaning. Additionally, fabrics treated with paraffin-based finishes are less permeable to air and vapour, resulting in a poorer wear comfort unless further refinement of the finishing occurs. Wash resistance, breathability, and soft handling can be improved by adding cross-linking agents such as isocyanates for fixation on the fibre. This technology is used in some commercial products.

Products consisting of solely paraffin and/or wax (bee wax) are also available as consumer impregnation products for outdoor clothing (e.g. Fjällraven Greenland Wax[3]).

Paraffinic emulsion repellents can be applied by both padding and bath exhaustion finishing processes (ZDHC, 2012; both processes are wet processes).

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[3] http://www.fjallraven.com/guides/material-guides/greenland-wax

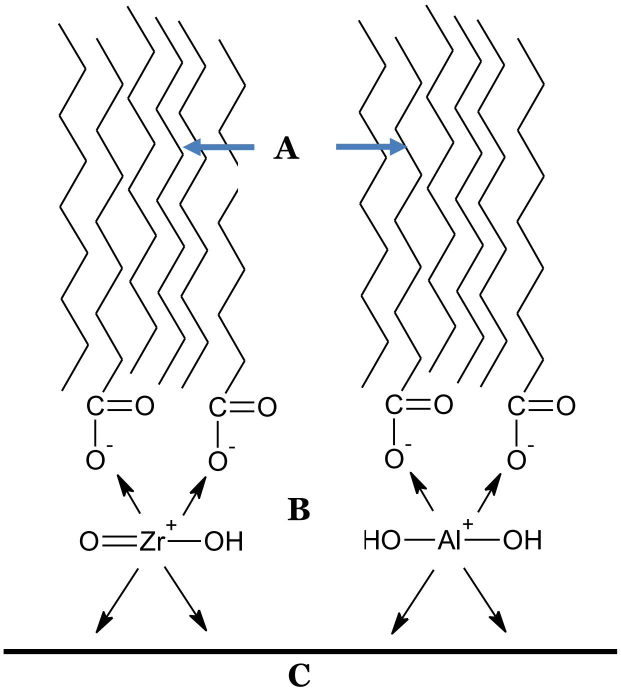
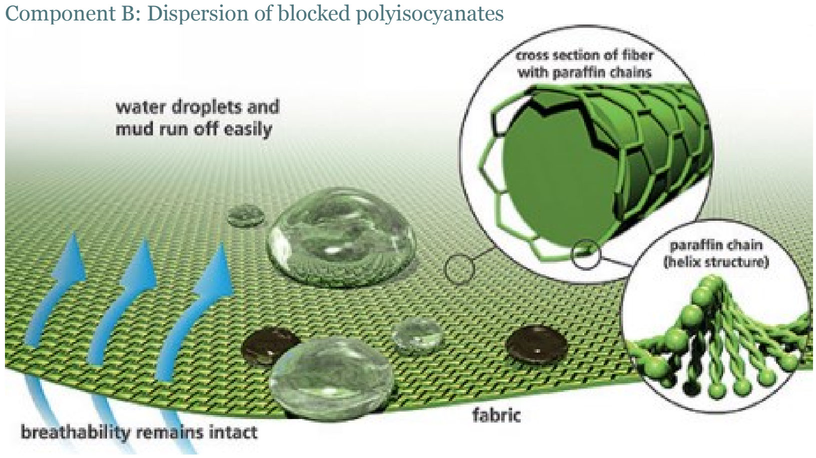


FIGURE 1.
EXAMPLES OF A FATTY ACID METAL SALT ON A FIBRE SURFACE. A: HYDROPHOBIC INTERACTIONS, B: POLAR INTERACTIONS, C: FIBRE SURFACE (BASED ON SCHINDLER AND HAUSER, 2004)

3.2 Examples of marketed products

Examples of marketed, paraffin-based products for which data have been received are shown below. Other marketed products for which detailed data have not been obtained include Texfin® HTF from Texchem®, zeroF from the German company CHT/Bezema and Itoguard NFC from LJ Specialities. The details on classification, environmental and health properties given in the tables below apply to the product (or, if specified, the components of the product) and not to single ingredients of the product/component.

Schoeller Textil AG	
Product name	ecorepel®
Chemical properties	Two component system: Component A: Dispersion of paraffins and fatty acid modified melamine resin. This component corresponds to separately marketed product: Schoeller protec-FF. Component B: Dispersion of blocked polyisocyanates  *Source: Schoeller Technologies AG*

Schoeller Textil AG	
Functional properties	• Water repelling. The ecorepel® finish can be optimized to ensure passage of the Raintest AATCC Test Method 35-2006. • Watery dirt such as sludge and mud are much less able to adhere to the fabric • Complies with the bluesign® standard and passes Oeko®-Tex Standard 100. • No effect on breathability (in accordance with ISO 11092). • Abrasion resistant: No effect on the feel despite a high level of resistance to abrasion and chaffing (AATCC 22-1996/ISO 4920)
Application areas	Clothing and non-clothing, effective on many types of fibres and many blends (cotton, polyester, wool).
Application process	Padding, Coating, Foam, Spray, Garment
Wash resistance	Good washing resistance (min. 30 washing cycles at 40° C). Function can be easily reactivated in the dryer (no more ironing necessary); alternatively, line drying is also possible
Price	Cheaper than PFAS-based products
Information on release/emissions of the substance during use and/or wash	No data.
Classification of the product	No hazard classification according to EU directives
Human health properties	Component A: Acute oral toxicity : $LD_{50} > 2.000$ mg/kg (rat) Component B: Acute oral toxicity : $LD_{50} > 2.000$ mg/kg (rat) Mutagenicity: negative (Ames test) Not skin sensitizing (OECD 406)
Environmental fate properties	Components are easily biodegradable in accordance with OECD 302 B (80–100 %, precipitation effect 49 %). Component A: BOD_5 3 mg/g COD 861 mg/g TOC 20% Nitrogen content of 0.66% Component B: BOD_5 37 mg/g COD 610 mg/g TOC 22% Nitrogen content of 2.8%
Environmental effects properties	Component A: Crustacean toxicity (*Daphnia magna*): $LC_{50} > 100$ mg/l, 48 h Sewage sludge bacteria toxicity: $EC_{50} > 2000$ mg/l, 3 h (OECD 202, part 1) Component B: Fish toxicity (zebra fish): LC_0 10.000 mg/l, $LC_{50} > 10.000$ mg/l, 48 h (OECD 203)

Archroma Management GmbH	
Product name	Arkophob FFR liq
Chemical properties	Encapsulation wax technology. Hydrocarbon polymer dispersion. Mixture of linear and branched hydrocarbons, which are applied with a crosslinking component to the textile fibre, generating a surface film comparable with a fatty film. Weakly cationic.
Functional properties	• Durable water repellent, comparable to PFAS-based products • No oil-repellency • Good abrasion resistance (abrasion resistance of the fibre improved) • Bluesign approved and can pass the Oekotex standard • No yellowing • Soft handling
Application areas	Clothing and non-clothing textiles, suitable for most textiles. Mostly for outdoor wear.
Application process	by Pad-Dry-Cure process, or exhaust process (e.g. on yarn)
Wash resistance	Displays wash resistance after 20 wash cycles, but slightly less wash resistant compared to PFAS-based products (C_6).
Price	Comparable to PFAS-based products (the product is cheaper compared to a fluorocarbon, but the lower efficiency requires a higher dosage).
Information on release/emissions of the substance during use and/or wash	No data.
Classification	The product is not classified as dangerous according to EC Directives/the relevant national laws.
Human health properties	Acute oral toxicity : LD_{50} > 2.000 mg/kg (OECD Test Guideline 420) Irritant effect on skin : No skin irritation (OECD Test Guideline 404) Irritant effect on eyes : No eye irritation (OECD Test Guideline 405)
Environmental fate properties	Biodegradability : > 90 % (28 d, DOC decrease) (OECD Test Guideline 302B) COD: 650 mg/g - Based on the components. Bioaccumulation of the product: not tested. Mobility in soil: no data available Behaviour in environmental compartments: no data available Results of PBT and vPvB assessment: no data available
Environmental effects properties	Fish toxicity : LC_{50} > 100 mg/l (OECD Test Guideline 203) Bacteria toxicity : IC_{50} > 100 mg/l (OECD Test Guideline 209) No tests on *Daphnia* or algae.

Huntsmann, Phobotex product range				
Product name	Phobotex APK	Phobotex JVA	Phobotex RCO	Phobotex ZAN
Chemical properties	Paraffin dispersion containing aluminium salt. Cationic.	Dispersion of paraffin oils and a fat modified melamine resin. Nonionic/cationic.	Dispersion of paraffin wax and acrylic copolymer. Nonionic/cationic. Contains also: 7-13% oxydipropanol CAS: 25265-71-8 1-3% Polyoxyethylene stearyl ammonium chloride CAS: 68187-69-9	Paraffin dispersion containing zirconium salt. Cationic. Contains also 3-7% Zirconium acetate, CAS 4229-34-9
Functional properties	Water repellent	Water repellent Compatible with PFAS-based polymers for additional oil- and alcohol repellency	Water repellent	Water repellent high resistance to sublimation
Application areas	Water repellent finish of cellulose, wool, synthetic/cotton and synthetic qualities. Waterproof finish of cotton and synthetic/cotton camping articles and cotton tarpaulins.	Women's and men's outerwear, leisure wear, work wear, technical textiles		E. g. tent materials, tarpaulins, rainwear, linings and umbrellas
Application process	Padding, drying temperature: 110 – 130 °C	Padding, but exhaustion method is possible, too.		Padding, but exhaustion method is possible, too.
Wash resistance	Non-durable	Good durability to laundering		Non-durable
Price	No information	No information	No information	No information
Information on release/emissions of the substance during use and/or wash	No data.	No data.	No data.	No data.
Classification of the product	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.
Human health properties*	LD_{50} Oral Rat >2000 mg/kg, Eyes Non-irritant (Rabbit), Skin Non-irritant (Rabbit). (based on a product with comparable composition)	LD_{50} Oral Rat >2000 mg/kg, Skin Mouse Not sensitizing	No data.	LD_{50} Oral Rat >2000 mg/kg Eyes Non-irritant (Rabbit), Skin Non-irritant (Rabbit).
Environmental fate properties*	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent 28days (DOC)) BOD_5 15 mg/g COD 420 mg/g TOC 19 % PBT: Not applicable	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent – 1 days (DOC)) Conclusion: Eliminated by adsorption onto effluent treatment sludge BOD_5 3 mg/g COD 861 mg/g TOC 20 %	No data.	Biodegradability: Inherent (OECD 302B modified, 80 to 100% Inherent 28 days (DOC)) BOD_5 21 mg/g COD 890 mg/g TOC 24 % PBT: Not applicable

Huntsmann, Phobotex product range				
Product name	Phobotex APK	Phobotex JVA	Phobotex RCO	Phobotex ZAN
		PBT: Not applicable		
Environmental effects properties*	Acute LC$_{50}$ >300 mg/l (Bacteria, 3 hours), Acute LC$_0$ 1000 mg/l (Rainbow trout, 48 hours, OECD 203), Acute LC$_{50}$ > 1000 mg/l (Rainbow trout, 48 hours, OECD 203)	Acute EC$_{50}$ >2000 mg/l (Bacteria, 3 hours), Acute LC$_{50}$ >100 mg/l (*Daphnia*, 48 hours, OECD 202 Part 1)	No data.	Acute IC$_{50}$ >300 mg/l (Bacteria, 3 hours), Acute LC$_0$ 1000 mg/l (Rainbow trout, 48 hours, OECD 203), Acute LC$_{50}$ > 1000 mg/l (Rainbow trout, 48 hours, OECD 203)

* Further toxicity data for single compounds are available in some cases. Here only data for the whole product are included.

3.3 Health assessment

3.3.1 Health data on specific impregnation agents

The ecorepel® product is based on long paraffin chains that wrap themselves, spiral-like, around the individual fibres, filaments or yarns in a very fine film. A sophisticated docking system binds them to the fibres. The honeycomb-like paraffin structures consist of hydrocarbon chains that are arranged over the whole area and reduce the surface tension. Water droplets and even mud with significantly higher surface tension simply run off. No hazard classification of the product according to EU directives. It is a two-component product.
Component A is a dispersion of paraffin- and fatty acid-modified melamine resin. The acute oral toxicity in rats is LD$_{50}$ > 2.000 mg/kg.
Component B is a dispersion of blocked polyisocyanates. The acute oral toxicity is LD$_{50}$ > 2.000 mg/kg (rat). The mutagenicity is negative (Ames test). It is not skin sensitizing (OECD 406).

Schoeller protec-FF is a dispersion of a fat modified melamine resin and paraffin oils similar to component A in Ecorepel. The substances are not further specified. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD$_{50}$ is > 2 g/kg, meaning no acute toxicity in rats, as well as no skin- or eye irritation.

Arkophob FFR liq is a polymeric dispersion (liquid wax) of unknown composition; it is water repellent only. The producer claims that the product should not be classified or labelled as dangerous according to EC Directives/the relevant national laws. As a polymer, this may be true, but the first-aid measures mentioned in the MSDS do not indicate a totally harmless chemical. The product has an acute oral toxicity: LD$_{50}$ > 2.000 mg/kg (OECD Test Guideline 420). No irritation of skin and eyes were observed.

PHOBOTEX®APK is a liquid paraffin wax dispersion containing aluminium salt; this normally is applied by padding. In the SDS, it is stated that the product is not hazardous and not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD$_{50}$ is > 2 g/kg; therefore, there is no acute toxicity in rats. No skin- or eye irritation is observed. It is, however, mentioned that: “This product contains substances for which Chemical Safety Assessments are still required”. On this basis, it is difficult to accept that the product presents no hazards.

PHOBOTEX®JVA Hydrophobic Agent is a dispersion of a fat modified melamine resin and paraffin oils. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD$_{50}$ is > 2 g/kg; therefore, there is no acute toxicity in rats. No skin or eye irritation is observed. In general, there is insufficient information for a health evaluation of this product.

PHOBOTEX®RCO is a dispersion of paraffin wax and an acrylic copolymer. The product is not classified as dangerous according to Directive 1999/45/EC and its amendments. However, according to the SDS it contains materials which may cause damage to the kidneys and central nervous system (CNS).

The product contains 7-13 % of dipropylene glycol/oxydipropanol with CAS no 25265-71-8/EC No. 246-770-3.It should be considered that glycol ethers generally have easy skin absorption/penetration. Most notifications in REACH about classification and labelling, according to CLP criteria, conclude that no classification of oxydipropanol was necessary. However, some notifiers proposed classifications as skin and eye irritants for H315 and H 319. Oxydipropanol has a registration dossier in REACH both on its own and in mixtures (ECHA, 2014a). The oral rat LD_{50} for oxydipropanol is 5 g/kg; therefore there would be no acute toxicity in rats. The $^{4h}LC_{50}$ was > 2.34 mg/L air. No skin- or eye irritation or sensitization in humans. In a repeated exposure study, rats were exposed to the glycol orally via drinking water for 105 weeks. The no observable adverse effect level (NOAEL) for liver effects was 470-530 mg/kg bw/d, high dosages. It must be emphasised that glycol ethers often are more toxic to humans than to experimental animals. Mutagenicity- and carcinogenicity tests were also negative.

The product also contains 1-3 % of CAS no. 68187-69-9: Polyoxyethylene stearylammonium chloride, a chemical which is self-classified as skin and eye irritating. It belongs to the important group of ethoxylated quaternary ammonium compounds.

PHOBOTEX®RCO: Dispersion of paraffin wax and acrylic copolymer, also containing 7-13% oxydipropanol, CAS: 25265-71-8 and 1-3% polyoxyethylene stearyl ammonium chloride. The CAS number is 68187-69-9. There is no data available on toxicity.

PHOBOTEX®ZAN Hydrophobic Agent is a paraffin dispersion containing zirconium acetate. It functions by cross-linking between textile substrates and films of water-repellent wax. Zirconium substitutes aluminium and increases the durability of the textile impregnation. In addition zirconium has a function as a flame retardant in the textiles.

It is mentioned in the SDS that the product itself is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} *of the product* is > 2 g/kg; thus no acute toxicity occurs in rats, and surprisingly no skin- or eye irritation or sensitization is observed.

The product contains 7-13 % of zirconium (IV) acetate (CAS no. 4229-34-9/EC no. 224-179-1), which is classified by the EU as a skin and eye irritant. CLP:

- Skin Irrit. 2 (H315)
- Eye Irrit. 2 (H319)

There is an ECHA registration of zirconium acetate (ECHA, 2014b).

- A DNEL of 23 mg/m^3 has been developed for workers exposed long-term by inhalation.
- A DNEL of 3.33 mg/kg bw/day has been developed for workers exposed long-term via the dermal route.
- A DNEL of 5.8 mg/m^3 has been developed for general population exposed long-term by inhalation.
- A DNEL of 1.67 mg/kg bw/day has been developed for the general population exposed long-term via dermal or oral route.
- Oral rat LD_{50} = 4.1 g/kg bw.
- Skin rat LD_{50} > 2 g/kg bw.
- Intraperitoneal rat LD_{50} = 122 mg Zr/kg bw.
- Corrosive or severely irritant to the eye.
- Medium hazard for the eyes in the general population

- Zirconium acetate solution (22%) was considered to have the potential to cause corrosion *in vivo*.
- In rat studies the NOAEL for systemic-, reproductive- and developmental toxicity in rats was considered to be ≥1000 mg/kg bw/day for males and females.
- It is not mutagenic in Ames-Test or other short-term tests performed.

PHOBOTEX®RHW Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No further details are available about the chemical content. It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments.

The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation and sensitization are observed.

In the SDS it is also mentioned that the product "contains material, which may cause damage to the following organs: lungs, liver, and gastro-intestinal tract." In addition, exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure. Thus the product may still be a health hazard to exposed people.

PHOBOTEX®RSH Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No details are available about the chemical content. It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation and sensitization is observed.
In the SDS it is also mentioned that the product "contains material which may cause damage to the following organs: lungs, liver, and gastro-intestinal tract." In addition, exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure. Thus the product may be a health hazard to exposed people.

PHOBOTEX®RHP is a fluorine-free water repellent for textiles. It is an aqueous solution/-formulation of a modified resin of unknown composition. In the SDS it is stated that the product is not hazardous and not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity in rats. No skin- or eye irritation is observed.

However, it is also mentioned:

1. "Contains material which may cause damage to the following organs: lungs, liver, and gastrointestinal tract."
2. "Inhalation exposure to decomposition products may cause a health hazard. Serious effects may be delayed following exposure."
3. "This product contains substances for which Chemical Safety Assessments are still required".

The second point may indicate a risk for lung edema, a potentially fatal disease. Therefore, the potential health effects of using this product may be considerable.

PHOBOTEX®HSR Hydrophilic Stain Release Agent is a dispersion of a hydrophilic nonionic polymer normally applied by padding. No SDS and no toxicity information have been obtained.

3.3.2 Risk of dangerous substances in the treated textiles

Classification - The products in this group do not have a harmonised classification as dangerous according to the CLP Regulation (Regulation (EC) No 1272/2008).

However, some of the known ingredients appear to be harmful, but most of the ingredients are not declared. Based on available information, there are no CMR-substances or endocrine disruptors in these paraffin-type products.

3.3.3 Risk of formation of dangerous substances by degradation of cured repellents

No information, but not likely.

3.4 Environmental assessment

Paraffin oils are mixtures of long chain alkanes (linear aliphatic hydrocarbons). Paraffin-based water repellents for textiles have been used for a long time. They are used as liquid emulsions typically with resins or salts of fatty acids.

3.4.1 Environmental data on specific impregnation agents

The ecorepel® brand from Schoeller is a two-component product. Component A is a dispersion of paraffin oils and fatty acid modified melamine resin. Component B is a dispersion of blocked polyisocyanates. The latter may contain traces of reactive isocyanates, hydrolysed easily in the environment. Both components were easily biodegradable in the OECD 302B test. Component A has been tested in an aquatic toxicity test with the Crustacean *Daphnia magna* and had a low acute toxicity ($^{48h}LC_{50}$ > 100 mg/L). In another test (OECD 202) with sewage sludge bacteria, the $^{3h}EC_{50}$ for component A was very high (>2000 mg/L) indicating very low toxicity. Component B was tested in a fish acute toxicity test (OECD 203) with zebra fish. The result was a very low acute toxicity ($^{48h}LC_{50}$ > 10.000 mg/L).

Schoeller protec-FF® from Schoeller is a dispersion of paraffin oils and a fat modified melamine resin, similar to component A in Ecorepel. The composition is not specified further. The product is easily biodegradable in the OECD 302B test. The product has been tested in an aquatic toxicity test with the crustacean *Daphnia magna* and had a low acute toxicity ($^{48h}LC_{50}$ > 100 mg/L). In another test (OECD 202) with sewage sludge bacteria, the $^{3h}EC_{50}$ for the product was very high (>2000 mg/L) indicating very low effect/toxicity. According to the SDS the product is self-classified according to Directive 1999/45/EC as potentially harmful to the water environment.

Arkophob®FFR liq from ARCHROMA is a polymeric dispersion (liquid wax) of unknown composition but probably paraffin-based; it is water repellent only. According to the SDS the product is not to be classified as dangerous according to EC Directives/the relevant national laws. It is easily biodegradable in the OECD 302B test. but bioaccumulation was not studied. Two ecotoxicity tests have been undertaken. The LC_{50} in a fish toxicity test (OECD 203) was >100 mg/L, and the IC_{50} in a bacteria toxicity test (OECD209) was > 100 mg/L; therefore, the ecotoxicity of this product is low.

PHOBOTEX®APK is a liquid paraffin wax dispersion containing an unspecified concentration of an aluminium salt. According to the SDS this product is not classified according to EU legislation. It was easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with bacteria and fish. The acute $^{3h}IC_{50}$ for bacteria (type non-specified in the SDS) was >300 mg/L, and the $^{48h}LC_{50}$ for rainbow trout (*Oncorhynchus mykiss*) was > 1000 mg/L; therefore, in both instances the toxicity was low.

PHOBOTEX®JVA Hydrophobic Agent from Huntsman is a dispersion of paraffin oils and a fat modified melamine resin. It is likely similar to the Schoeller-Protec-FF product discussed above.

According to the SDS, this product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It is easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with non-specified bacteria with a $^{3h}IC_{50}$ > 2000 mg/L, and in an acute immobilisation test (OECD 202) with *Daphnia magna*, giving an $^{48h}EC_{50}$ > 100 mg/L; therefore, in both instances the toxicity was low.

PHOBOTEX®RCO is a dispersion of paraffin wax and an unknown acrylic copolymer. According to the SDS the product is not classified as dangerous according to Directive 1999/45/EC and its amendments.
The products contains 7-13 % of dipropylene glycol/oxydipropanol with CAS no. 25265-71-8/EC No. 246-770-3, which is not classified according to the CLP Directive but has a registration dossier in REACH (ECHA, 2014a). According to the registration dossier, oxydipropanol had a calculated atmospheric half-life of about 4 hrs, and it was easily biodegradable in a fresh water test but less biodegradable in sea water (OECD 306). In a test for bioaccumulation in fish (the common carp: *Cyprinus carpio*) (OECD 305C) the bioconcentration factor (BCF) was 0.3-4.6. The octanol-water partition coefficient log K_{oc} = -0.462. A EUSES model calculation determined the Henry's Law constant H at 12°C as 0.000907 Pa m^3/mol. A McKay distribution modelling exercise showed the relative percent distribution in media as 0.11% in air, 46.1 % in water, 53.7 % in soil and 0.08 % in sediment.

Oxydipropanol has been studied in several ecotoxicity tests:

- In a freshwater fish acute toxicity test with the goldfish (*Carassius auratus*) the $^{24h}LC_{50}$ was > 5000 mg/L
- in an acute immobilisation test (OECD 202) with *Daphnia magna* the $^{48h}EC_{50}$ was > 100 mg/L
- In an algae growth inhibition test (OECD 201) the $^{72h}EC_{50}$ was > 100 mg/L
- The substance initiates growth inhibition of the bacteria *Pseudomonas putida* at a concentration of 1000 mg/L
- The acute toxicity to an endangered frog species, *Rana porosa brevipoda,* inhabiting rice fields of western Japan, was determined as a $^{48h}LC_{50}$ = 5300 mg/L
- The acute toxicity in another frog species, *Xenopus laevis,* was $^{48h}LC_{50}$ = 3181 mg/L
- An avian acute oral toxicity test (EPA OPPTS 850.2100) the $^{14d}LD_{50}$ > 2000 mg/kg bw.

The conclusions of assessments of the hazard for oxydipropanol were:

- Freshwater organisms predicted no effect concentration (PNEC) = 0.1 mg/L with assessment factor 1000
- Marine water organisms PNEC = 0.01 mg/L with assessment factor 10000
- Intermittent releases PNEC = 1 mg/L with assessment factor 100
- Sewage treatment plant (STP) PNEC = 1000 mg/L with assessment factor 1
- Fresh water sediment PNEC = 0.238 mg/kg sediment dw
- Marine water sediment PNEC = 0.0238 mg/kg sediment dw
- Terrestrial organisms PNEC = 0.0253 mg/kg soil dw
- Predator secondary poisoning oral PNEC = 313 mg/kg food with assessment factor 3000.

The PHOBOTEX®RCO product also contains 1-3 % of CAS no. 68187-69-9: Polyoxyethylene stearylammonium chloride, a polymer which is classified in the CLP system as "Aquatic Chronic 3, with risk phrase: H412". The product has not been tested for biodegradation or in ecotoxicity tests.

PHOBOTEX® ZAN Hydrophobic Agent is a paraffin dispersion containing 7-13 % of zirconium (IV) acetate (CAS no. 4229-34-9/EC no. 224-179-1. According to the SDS, the product is not classified as dangerous as per Directive 1999/45/EC and its amendments. The product was easily biodegradable in a modified OECD 302B test. The product has been tested in acute ecotoxicity tests with bacteria and fish. The acute $^{3h}IC_{50}$ for bacteria (type not-specified in the SDS) was >300 mg/L, and the $^{48h}LC_{50}$ for rainbow trout (*Oncorhynchus mykiss*) was > 1000 mg/L; thus in both instances toxicity was low. The identical test results indicate a close relationship to the previously discussed PHOBOTEX®APK containing an aluminium salt instead of a zirconium salt. There is an ECHA registration of the water soluble zirconium acetate (ECHA, 2014b).

In a 28 day screening test with a closed bottle (OECD 301D); the organic part of zirconium acetate was ready biodegradable in water. Being a natural element, the zirconium metal itself cannot degrade. Transfer of zirconium-ions from soil to tomato- and pea plants was studied in two soils during a 7-day exposure period, but the uptake was very low; thus, the potential for accumulation in plants is low. The acute toxicity of zirconium acetate to rainbow trout (*Oncorhynchus mykiss*) was studied in an aquarium test, and a $^{7d}LC_{50}$ was determined to be 58.7 mg/L. In a Respiration Inhibition Test with Activated Sludge (OECD 209), the 3 hours the no observable effect concentration (NOEC) was 742 mg zirconium acetate/L fresh water. Some other studies should be discarded, because they used water-free zirconium acetate, which is not water soluble. The conclusion was that there was no potential for bioaccumulation or ecotoxicological effects by zirconium acetate.

PHOBOTEX®RHW Hydrophobic Agent is an aqueous solution of a modified resin used as a water repellent. No further details are provided about the chemical content. According to the SDS, the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12), the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna*, the result was a $^{48h}EC_{50}$ 1-10 mg/L; in the last instance, therefore, a significant toxicity was observed.

PHOBOTEX®RSH Hydrophobic Agent is an aqueous formulation of a modified resin used as a water repellent. No details are provided about the chemical content. The SDS mentions that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12), the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna*, the result was a $^{48h}EC_{50}$ 10-100 mg/L; therefore, in the last test the result showed this substance to be 10 times less toxic to *Daphnia* than the previously discussed PHOBOTEX®RHW.

PHOBOTEX® RHP is a fluorine-free water repellent for textiles. It is an aqueous solution/-formulation of a modified resin of unknown composition. The SDS mentions that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. It was easily biodegradable in a modified OECD 302B test. In an acute ecotoxicity test with luminescent bacteria (DIN 384 12) the $^{½h}EC_{50}$ was > 1000 mg/L. In an acute immobilisation test (OECD 202) with *Daphnia magna* the result was a $^{48h}EC_{50}$ 10-100 mg/L; therefore, these identical test results indicate a close relationship to the previously discussed PHOBOTEX®RSH.

PHOBOTEX® HSR Hydrophilic Stain Release Agent is a white dispersion of a hydrophilic non-ionic polymer. No details about the chemical content, and no SDS or other information about environmental fate properties and toxicity are available. Therefore the product cannot be evaluated.

3.4.2 Risk of releases of dangerous substances from treated textiles

The products in this group do not have a harmonised classification as dangerous according to the CLP Regulation (Regulation (EC) No 1272/2008).

However, some of the known ingredients appear to be harmful but most of the ingredients are not listed. Based on available information these products do not contain PBT substances which may be released during processing and washing. The products and the known ingredients seem to be easily biodegradable, having low to moderate acute toxicity to aquatic organisms.

3.5 Summary

Availability and technical properties - Many products are available and agents of this type have been on the market for many years. Used for clothing and non-clothing textiles, they are effective on many types of fibres and many blends. The agents provide durable water repellency but not oil repellency. For those products where the price indication is available, costs are comparable to PFAS-based agents (they are cheaper compared to the PFAS-based agents, but their lower efficiency requires a higher dosage).

Health assessment - The products in this group are liquid emulsions that, according to the producers, should not be classified as hazardous to health. However, some of the known ingredients appear to be harmful. The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which in pure form are harmless to human health. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.

Environmental assessment - The products in this group are liquid emulsions that according to the producers should not be classified as hazardous for the environment. The main known ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which in pure form are readily biodegradable, not bioconcentrated or accumulated in organisms and food chains. The toxicity to aquatic and terrestrial organisms is low even at concentrations above water solubility.

Main data gaps - More information about the composition of the products and the environmental and health properties of the ingredients is needed. For two-component products, more information is needed about the reaction product.

More information about the composition of the products and the environmental properties of the product and ingredients is needed. For two-component products, more information is needed for the fate of the reaction product.

There are few studies available regarding the products and ingredients that are of acute toxicity to terrestrial organisms, their chronic ecotoxicity in general, and their potential for bioaccumulation.

4. Silicone repellent chemistries

4.1 Chemistry

Polydimethylsiloxanes are the most common silicone repellents. Due to their structure, they form hydrogen bonds with fibres and exhibit repellency effects on the outer surface of fibres (ZDHC, 2012). See figure 2.

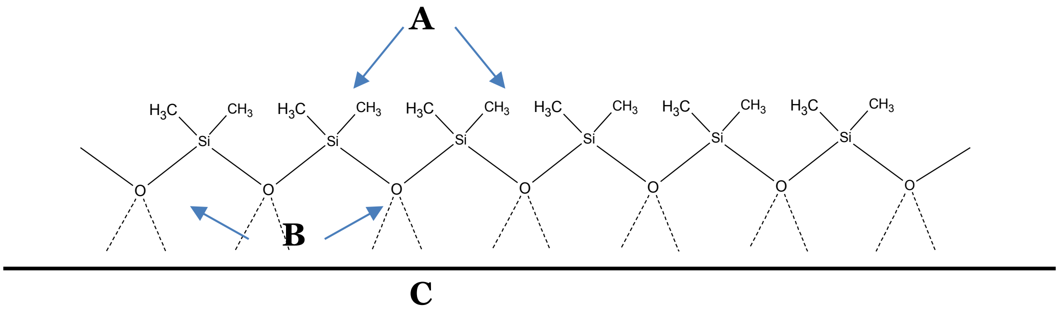


FIGURE 2
POLYDIMETHYLSILOXANE ON A FIBRE SURFACE. A – HYDROPHOBIC SURFACE, B – HYDROGEN BONDS TO POLAR SURFACE, C – FIBRE SURFACE (BASED ON SCHINDLER AND HAUSER, 2004)

Silicone repellents designed to be durable finishes generally consist of a polymer, silandiol, a polymer methyl silane, and a catalyst, e.g. tin octanoate. The silandiol and silane components react to form a three-dimensional cross-linked sheath around the fibres and the catalyst promotes alignment of the silicone film on the fibre surface (Figure 3). The methyl groups of the silicone polymer are positioned outwards and produce the water repellent effects. Hydrogen bonding between the polymer and textile surface, e.g. cellulose, provides fixation to the fibre (Schindler and Hauser, 2004; ZDHC, 2012).

Silicon repellents offer a high degree of water repellency at relatively low concentrations. Application of excess amounts, however, can reduce the water repelling effects. Silicon repellents have moderate durability for laundering and dry cleaning, because of possible hydrolysis of the siloxanes and rupture of the surface film, which can be caused by cellulose swelling. They provide no oil repellency. Waste waters, particularly from residual baths of the finish application processes, are mentioned to be toxic to fish (ZDHC, 2012).

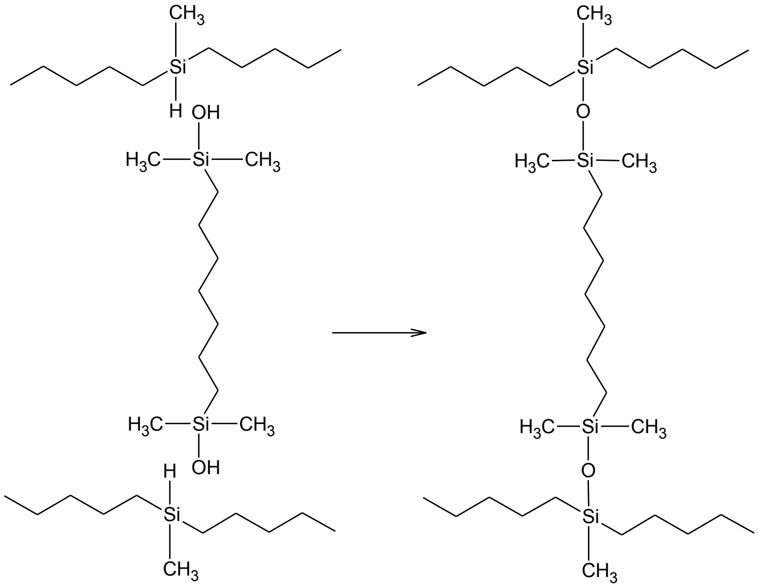
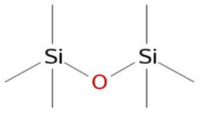
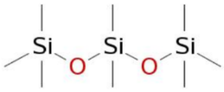
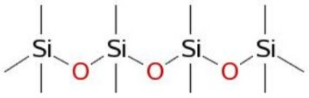
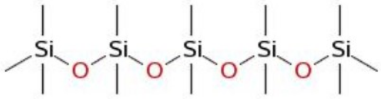
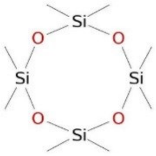
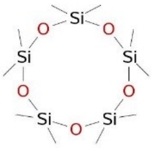
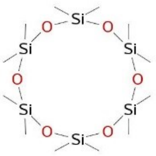


FIGURE 3
SILANOL-SILANE REACTION. A – CROSSLINKING BY REMOVAL OF H2, B – THE CROSSLINKED SI-O-SI POLYMER. TIN OCTOATE CATALYSES THE REACTION (BASED ON SCHINDLER AND HAUSER, 2004)

The following siloxanes, used as intermediates for polymer synthesis, and silicone polymers, used for textile impregnation (shown in Table 4) have been discussed in a background report on PFOS substitutes developed for the UNEP POPs Review Committee (UNEP, 2013).

TABLE 4
SILOXANES AND SILICONE POLYMERS (FROM UNEP, 2013)

Abbreviation	Name	Cas no.	Structure*
HMDSO	Hexamethyl disiloxane	107-46-0	 *
MDM	Octamethyl trisiloxane	107-51-7	 *
MD2M	Decamethyl tetrasiloxane	141-62-8	 *
MD3M	Dodecamethyl pentasiloxane	141-63-9	 *
D4	Octamethyl cyclotetrasiloxane	556-67-2	 **
D5	Decamethyl cyclopentasiloxane	541-02-6	 **
D6	Dodecamethyl cyclohexasiloxane	540-97-6	 **

* Chemical structures from http://esis.jrc.ec.europa.eu/.
** Chemical structures from registrations at ECHAs dissemination tool.

4.1.1 Other uses of silicon technology

Sometimes siloxane-based textile repellents are used along with the classic cationic textile surfactant 1-(stearamidomethyl) pyridinium chloride (below) – occasionally together with carbamide (urea) and melamine resins.

The dendrimer repellent chemistry described in section 5 includes the use of organopolysiloxane chemistry, but the chemistry of these repellents is essentially different from the silicones.

4.2 Examples of marketed products

Repellents based on silicone chemistry have been used for many years, and many products incorporating it are marketed.

Examples of marketed products and product details regarding classification, environmental and health properties are shown below. Other marketed products for which detailed data have not been obtained include Texfin®-HTF and Texfin®-SWR-A from Texchem, but many different brands are marketed.

Huntsman - part of Phobotex series			
Product name	**Phobotex Catalyst BC**	**Phobotex SSR**	**Phobotex WS Conc**
Chemical properties	Emulsion of polydimethylsiloxane and a self-crosslinking condensation product. Cationic Contains also 1-3% Alcohols, C_{11-14}-iso-, C_{13}-rich CAS: 68526-86-3	Dispersion containing hydrophilic polysiloxane and hydrophilic polyester. Nonionic.	Polysiloxane-based emulsion. Contains also 3-7% Cocoalkyl bis(2-hydroxyethyl) ethoxylated methyl ammonium chloride (no CAS, polymer)
Functional properties	Water repellent stability to weathering including UV light	Water repellent Antistatic finishing on synthetic fibres	Water repellent Increases fabric resilience
Application areas		Synthetic fibres and their blends	Pile, velvet fabrics and casual outerwear
Application process	Padding only	Padding	Padding only Should be applied together with Phobotex® Catalyst BC
Wash resistance	Good durability to laundering	Very high durability to washing, particularly on polyester and aramid fibres	Good durability to laundering
Price	No data.	No data.	No data.
Information on release/emissions of the substance during use and/or wash	No data.	No data.	No data.
Classification of the product	R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.	The product is not classified as dangerous according to Directive 1999/45/EC and its amendments.	Xi; R41 - Risk of serious damage to eyes R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
Human health properties*	LD_{50} Oral Rat >2000 mg/kg Eyes – Non-irritant. Rabbit Skin - Non-irritant. Rabbit	LD_{50} Oral Rat >2000 mg/kg Eyes Non-irritant (Species not known), Skin Non-irritant (Species not known).	LD_{50} Oral Rat >2000 mg/kg Eyes Irritant (Species not known), Skin Non-irritant (Rabbit).
Environmental fate properties*	Biodegradability: Not readily (OECD 303A modified, 25 to 50 % - 28 days (TOC)) BOD_5 15 mg/g COD 820 mg/g TOC 18 % PBT: Not applicable	Biodegradability: Eliminated by adsorption onto effluent treatment sludge (OECD 302B modified, 60 to 80%, 28days (DOC)) BOD_5 5 mg/g COD 317 mg/g TOC 10 % PBT: Not applicable	Biodegradability: Not readily (OECD 303A modified 50 to 100%, 28days (TOC)) BOD_5 60 mg/g COD 4780 mg/g TOC 14 % PBT: Not applicable

Huntsman - part of Phobotex series			
Product name	**Phobotex Catalyst BC**	**Phobotex SSR**	**Phobotex WS Conc**
Environmental effect properties*	Acute IC_{50} >300 mg/l (Bacteria, 3 h) Acute LCo 20 mg/l (Fish - Rainbow trout 48 hours, OECD 203) Acute LC_{50} 45 mg/l (Fish - Rainbow trout, 48 hours, OECD 203)	Acute EC_{50} >5000 mg/l (Bacteria Luminescent, DIN 38412 Lumistox test, 30 min) Acute IC_{50} >300 mg/l (Wastewater bacteria, 3 h) Acute LC_0 1000 mg/l (Rainbow trout, 48 h, OECD 203) Acute LC_{50} >1000 mg/l (Rainbow trout, 48 h, OECD 203)	Acute EC_{50} 100 mg/l (Daphnia, 48 h) Acute IC_{50} >300 mg/l (Bacteria, 3 h) Acute LC_0 20 mg/l (Rainbow trout, 48 h, OECD 203) Acute LC_{50} 45 mg/l (Rainbow trout, 48 h, OECD 203)

Bluestar Silicones - RHODORSIL TCS 7001	
Product name	RHODORSIL TCS 7001
Chemical properties	Alkyl polysiloxane solution in solvent phase (solvent: aliphatic hydrocarbon), contains 95% hydrocarbons, C_9-C_{10}, *n*-alkanes, isoalkanes, cyclics, <2% aromatics (EC No. 927-241-2) and <2 % naphtha (EC No. 265-150-3)
Functional properties	• Waterproofing to natural fabrics, synthetic fabrics, synthetic leathers. • Outstanding abrasion resistance in humid environments • Resistance to detergent washing
Application areas	Outdoor fabrics - natural and synthetic leathers. Aerosols for reproofing of fabrics and leathers (natural and synthetic).
Application process	Spray or impregnation waterproofing of fabrics and leathers. When using aerosols: it is recommended to use butane gas type propellant. In the case of fabric impregnation it is recommended to heat it for 3 minutes at a temperature of 150°C
Wash resistance	No data.
Price	Possibly less expensive than PFAS-based agents
Information on release/emissions of the substance during use and/or wash	No data.
Classification of the product	Classification according to Directive 67/548/EEC or 1999/45/EC as amended: R10 Xn; R65 R66 R67 R52/53 (corresponding to Aquatic Chronic 3;H412, Flam. Liq. 3;H226, STOT SE 3; H336, Skin Irrit. 3; H316, Asp. Tox. 1; H304)
Human health properties	No data.
Environmental fate properties	The product has the potential to bioaccumulate. Otherwise no data.
Environmental effects properties	No data.

4.3 Health assessment

4.3.1 Health data on specific impregnation agents

PHOBOTEX® CATALYST BC Hydrophobic Agent is an emulsion of a polydimethyl siloxane and a self-crosslinking cationic condensation product. It is volatile. The product is classified as harmful for aquatic organisms according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} for the product was > 2 g/kg. Regarding toxicity see above.

The product contains 1-3% of CAS no. 68526-86-3/EU no. 271-235-6: Isotridecyl alcohol (mixed)/11-methyldodecan-1-ol, which is registered in REACH (ECHA, 2014l). The following DNELs are mentioned for this alcohol:

Long term	Inhalation	293.86 mg/m^3	Workers Systemic
Long term	Dermal	416.67 mg/kg bw/d	Workers Systemic
Long term	Inhalation	89.96 mg/m^3	Consumers Systemic
Long term	Dermal	250 mg/kg bw/d	Consumers Systemic
Long term	Oral	25 mg/kg bw/d	Consumers Systemic

The oral rat LD_{50} for isotridecyl alcohol was > 2 g/kg and the rat inhalation $^{6h}LC_{50}$ >12.2 mg/L; therefore there is no acute toxicity in rats. No skin- or eye irritation is observed. The alcohol was also negative in the three mutagenicity studies performed. In a study with rats dosed orally with the alcohol for 14 days, the NOAEL was 130 mg/kg bw/day. In a teratogenicity study with rats exposed for 10 days, the NOAEL was 100 mg/kg bw/day. These NOAEL values are of the same magnitude as the PFAS it substitutes, and this substance should be considered harmful.

PHOBOTEX® SSR Soft Stain Release Agent is a dispersion of hydrophilic polyester (polymer) with a functional polysiloxane. No further details from the SDS/TDS are available about the chemical content.

It is mentioned in the SDS that the product is not classified as dangerous according to Directive 1999/45/EC and its amendments. The oral rat LD_{50} is > 2 g/kg; therefore there is no acute toxicity of the product in rats. No skin- or eye irritation and sensitization is observed.

PHOBOTEX® WS CONC. Hydrophobic Agent is a non-ionic polysiloxane based emulsion. According to the SDS the product is classified as an irritant according to Directive 1999/45/EC and its amendments. The major human health hazard is: “Risk of serious damage to eyes”.
The oral rat LD_{50} *of the product* is > 2 g/kg; therefore there is no acute toxicity in rats.

The product contains 3-7% of the quaternary ammonium compound and emulsifier: Cocoalkylbis(2-hydroxyethyl) ethoxylated methylammonium chloride/ *N,N*-Diethoxylated-*N*-coco-*N*-methylammonium chloride (CAS no. 61791-10-4), which is pre-registered in ECHA (ECHA, 2014c). This *substance* has a rat oral LD_{50} = 580 mg/kg bw (ChemIDplus, 2014), and it is a powerful irritant for skin and especially eyes (CEFIC, 2006). Therefore, the SDS understates the hazard from the product.

For **OC-aquasil Tex W™, OC-aquasil Tex N™** no detailed information is available, other than that the product contains <10.5% an organic silicon compound and <5% of an organic acid. The product is not classified according to 1999/45/EC. It is stated that the product contained no substances that were classified as carcinogenic, mutagenic or toxic for reproduction.
However, the organosilicon compound is classified as skin irritating, group 2 (H315). The organic silicon compound (in concentrated form) had an oral rat LD_{50} > 5000 mg/kg. The organic acid is also classified as skin irritating, group 2 (H315). In addition, it is classified as eye irritating, group 2 (H319), and has specific target organ toxicity by single exposure in category 3 (STOT SE 3) (H335). In concentrated form it has LD_{50} (mouse) > 1500 mg/kg.

RHODORSIL/Bluesil TCS 7001 is an alkyl polysiloxane solution in a solvent phase. Classification has been done according to Directive 67/548/EEC or 1999/45/EC as amended: R10 Xn; R65 R66 R67 R52/53. No human health data are available.

4.3.2 Risk of dangerous substances in the treated textiles

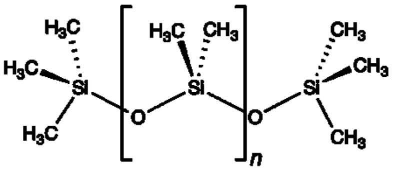
For most of the alternative products reviewed there is insufficient qualitative and quantitative public information available about the ingredients. Most products do not have information available because they are protected by trade secrets.. For some siloxanes used as intermediates in production of silicon polymers, much health and environmental information exists but it is unclear to what degree these siloxanes are ingredients or impurities in the commercial products or are present in the textiles.

Various siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, are used as intermediates for synthesis of silicone polymers, which in turn is used for *inter alia* textile impregnation (Gravier et al., 2003). As an example, according to one of the producers, D4 is used as a monomer ('building block') in the production of silicone polymers which may be oils, greases, rubbers and resins. Furthermore, it is used as an intermediate (starting material) in the production of other organosilicon substances (Momentive 2014).

4.3.3 Health assessment of siloxanes

Polydimethylsiloxanes (PDMS)

Some years ago linear polydimethylsiloxanes (PDMS ,CAS No. 63148-62-9) - a type of non-volatile (odourless), fluid (viscous) "silicones" - were evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC, 2011).



PDMS

Humans may be exposed to PDMS via oral ingestion and dermal contact. In laboratory animals, PDMS had a low potential for absorption via these routes. Swallowed PDMS is rapidly excreted unchanged in the faeces. Aerosolised PDMS may give rise to inhalation exposure, but there is no indication of any adverse effects. PDMS is not a skin irritant or a skin sensitizer, and it is only mildly to non-irritating to the eyes.

1. Acute and repeated dose toxicity studies conducted in laboratory animals on PDMS of different viscosities do not show any significant adverse effects. Long-term chronic/carcinogenicity and reproductive toxicity studies were also without adverse effects. PDMS is not mutagenic *in vitro*.
2. In humans, PDMS has no effect on the immune system. PDMS is used in urology, ophthalmology and dermatology (skin correction). Autoimmune disorders (e.g. scleroderma) cannot be linked to PDMS. Several human diseases (connective tissue, atypical connective tissue, rheumatic and autoimmune diseases, and breast cancer) have been reported after injection of PDMS (for cosmetic purposes) or placement of breast implants (made of high viscosity PDMS). These diseases are, however, not associated with PDMS.

Low-molecular-weight poly(dimethylsiloxanes)

Low-molecular-weight poly(dimethylsiloxanes) (MM, MDM, MD2M and MD3M) are used as intermediates in the synthesis of silicone polymers, but no data on the trace levels of low-molecular-weight poly(dimethylsiloxanes) in the final fabric are available.

Detailed health data for the low-molecular-weight poly(dimethylsiloxanes) from the REACH registration dossiers, available from ECHA's Dissemination Site Database (ECHA 2014, b), are shown in Appendix 1.

Low-molecular-weight poly(dimethylsiloxanes) have been studied by siloxane manufacturers, and they conclude that the poly(dimethylsiloxanes) studied all possess a very low potential for toxicity. Further information on HMDSO is included along with the description of the cycling siloxanes below.

Cyclic siloxanes
The cyclic siloxanes may be used as intermediates in the synthesis of silicone polymers, but no data on the trace levels of cyclic siloxanes in the final fabric is available.

Detailed health data for the cyclic siloxanes (D4, D5, D6) from the REACH registration dossiers, available from ECHA's Dissemination Site Database (ECHA 2014, b), are shown in Appendix 1.

In a study for the Danish EPA, the toxicological information which primarily existed for D4, D5 and HMDSO was reviewed (Lassen et al., 2005). The three siloxanes demonstrate a relatively low order of acute toxicity by oral, dermal and inhalation routes and do not require EU classification for this effect. They are not shown to be irritating to skin or eyes and are also not found to be sensitizing by skin contact. Data on respiratory sensitization have not been identified.

Sub-acute and sub-chronic toxicity studies show that the liver is the main target organ for D4, whereby hepatocellular enzymes are induced. This enzyme induction contributes to the elimination of the substance from the tissues. This enzyme induction contributes to the elimination of the substance from the tissues.

D5 has a similar liver enzyme induction profile as D4 but the primary target organ for D5 exposure by inhalation was the lung.

In sub-acute and sub-chronic inhalation studies with rats of HMDSO affects in particular the lungs and kidneys, which are the target organs.

None of the investigated siloxanes show any signs of genotoxic effects *in vitro* or *in vivo*. However, preliminary results indicate that D5 may induce uterine tumours in female rats, and this carcinogenic effect is considered the critical effect for D5 (US EPA, 2005).

Inhalation of D4 impaired fertility in rats, and that was considered the critical effect. D4 was also classified as a substance toxic to reproduction in category 3 with the risk phrase R62 ('Possible risk of impaired fertility').

The results of a study to screen for estrogenic activity indicated that D4 had both a very weak estrogenic and anti-estrogenic activity. Comparison of the estrogenic potency of D4 relative to ethinylestradiol (steroid hormone used in p-pills) indicated that D4 is 585,000 times less potent than ethinylestradiol in the rat and 3.7 million times less potent than ethinylestradiol in the Fisher-344 rat strain

A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air. Toxic effects of D3, D4, D5, D6 and HMDSO were studied using a “read-across” modelling method based on structural similarity and its relation to toxicity. The linear siloxane HMDSO appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also observed. An ambient quality criterion of 0.01 mg/m³ was derived based on lung toxicity, including a safety factor of 250 (Greve et al., 2008).

The Scientific Committee on Consumer Products in the European Union has published an Opinion on D4 and D5 in which the safety of D4's use as a cosmetic ingredient was not questioned (SCCP, 2010).

In the United States, the Cosmetic Ingredient Review (CIR) panel has published an assessment of the safety of cyclic siloxanes: D3, D4, D5, D6 and D7. The panel concluded that D4, D5, D6 and D7 were safe for use in cosmetics, but D3 will be taken off the International Nomenclature of Cosmetic Ingredients (INCI) list, because it was not a commercial product (Johnson et al., 2011).

Other studies of siloxanes, however, indicate that they appear to be harmful when inhaled, and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact with the product WorléeAdd® 340 may cause skin irritation. In short, knowledge of the toxicity of siloxanes is still incomplete.

Some siloxanes are metabolized and the metabolites (hydroxylation metabolites) are expected to be found in blood and urine. California State EPA notes the weak estrogenic activity of D4 combined with long half-life and uterine tumours resulting from D5 exposure. The California State EPA also noted that cyclosiloxanes appeared to have long half lives in people (California EPA, 2008).

4.3.4 Classification of siloxanes

The harmonised classification according to the CLP Regulation (Regulation (EC) No 1272/2008) and the classification as notified to the C&L inventory is indicated in the table below.

TABLE 5
HARMONISED CLASSIFICATION AND CLASSIFICATION INFORMATION NOTIFIED BY MANUFACTURERS AND IMPORTERS (C&L INVENTORY)

Substance	**CAS No**	**Harmonised classification * C&L List (ECHA; 2014D)**		
		Hazard Class and Category Code(s)	**Hazard Statement Codes**	**Number of notifiers**
Polydimethylsiloxanes (PDMS)	63148-62-9	**Total**		**1405**
		Not classified		
		Aquatic chronic 4	H413	356
		Eye Irrit. 2	H319	131
		Aquatic chronic 2	H411	51
		Repr. 2	H361	13
		Flam. liq. 3	H226	25
		Skin corr. 1A	H314	13
		Eye dam. 1	H318	13
		Asp. tox. 1	H304	1
		Acute tox. 1	H300	1
		Acute tox. 2	H300	1
Octamethylcyclo-tetrasiloxane (D4)	556-67-2	Repr. 2 Aquatic chronic 4	H361f H413	Harmonised classification*

Substance	CAS No	Harmonised classification * C&L List (ECHA; 2014D)		
		Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
Decamethylcyclopentasiloxane (D5)	541-02-6	**Total**		**1479**
		Not classified		1313
		Aquatic chronic 4	H413	65
		Acute tox. 3	H331	46
		Skin irrit. 2	H315	27
		Eye irrit. 2	H319	31
		STOT SE 3	H335	2
Dodecamethylcyclohexasiloxane (D6)	540-97-6	**Total**		**266**
		Not classified		230
		Eye Irrit. 2	H319	19
		Aquatic chronic 4	H413	16
Octamethyltrisiloxane (MDM)	107-51-7	**Total**		**224**
		Not Classified		83
		Flam. liq. 3	H226	141
		Aquatic chronic	H413	3
Hexamethyldisiloxane (HMDSO)	107-46-0	**Total**		**924**
		Not classified		99
		Flam. liq. 2	H225	793
		Aquatic acute 1	H400	596
		Aquatic chronic 1	H410	408
		Carc. 2	H351	63
		Aquatic chronic 2	H411	73
		Acute tox. 3	H301	18
		Acute tox. 4	H332	18
		Flam sol. 1	H228	1
		Water react. 1	H260	1
		Eye irrit. 2	H319	1
		Flam liq. 3	H226	1
		Asp. tox. 1	H304	1
		Skin irrit. 1	H315	1

* According to Annex VI of Regulation (EC) NO 1272/2008 (CLP REGULATION).

4.4 Environmental assessment

4.4.1 Environmental data on specific impregnation products

PHOBOTEX®CATALYST BC Hydrophobic Agent from Huntsman is an emulsion of a PDMS and a self-crosslinking cationic condensation product. According to the SDS the product is classified as harmful for aquatic organisms and may cause long-term adverse effects in the aquatic environment (R52/R53) according to Directive 1999/45/EC and its amendments. In addition, the following safety phrase S61 applies: "Avoid release to the environment. Refer to special instructions/safety data sheet." The product has a low acute toxicity to bacteria with a $^{3h}IC_{50}$ >300 mg/L, but a higher toxicity to rainbow trout (*Oncorhynchus mykiss*) with a $^{48h}LC_{50}$ = 45 mg/L. The product was somewhat biodegradable (25-50 % in 28 days) in a test system (OECD 303A).

The product contains 1-3% of CAS no. 68526-86-3/EU no. 271-235-6: Isotridecyl alcohol (mixed)/11-methyldodecan-1-ol, which is classified harmful (N, R50; Aquatic Acute 1, H400) to the environment and registered in REACH (ECHA, 2014l).

Isotridecyl alcohol is easily biodegradable (>60%) in activated sludge over 28 days. It is also readily biodegradable in water (OECD 301F). The octanol-water partition coefficient is 5.4 (log K_{ow}) at 25°C. In a bioaccumulation test in rainbow trout (O*ncorhynchus mykiss*), according to OECD 305, the BCF was 30-60. Isotridecyl alcohol has a low potential to bioaccumulate in fish tissue. The BMF was even lower at 0.01. In an acute toxicity test with freshwater fish (OECD203), the $^{96h}LC_{50}$ was 0.42 mg/L to rainbow trout (O*ncorhynchus mykiss*). In an algae test with *Pseudokirchneriella subcapitata* the chronic $^{72h}NOEC$ was 1.5 mg/L and $^{72h}EC_{50}$ = 2.6-3.2 mg/L.

The conclusions of assessments of the hazard for isotridecyl alcohol were:

- Fresh water organism PNEC = 0.03 mg/l with assessment factor 1
- Marine water organism PNEC = 0.0003 mg/l with assessment factor 100
- Intermittent releases PNEC = 0.0022 mg/l with assessment factor 100
- STP PNEC = 105.3 mg/L with assessment factor 1
- Fresh water sediment PNEC = 115.6 mg/kg sediment dw with assessment factor 1
- Marine water sediment PNEC = 1.156mg/kg sediment dw with assessment factor 100
- Terrestrial organisms PNEC = 93.7 mg/kg soil dw with assessment factor 1
- Predator secondary poisoning oral PNEC = 22.22 mg/kg food with assessment factor 90.

PHOBOTEX®SSR Soft Stain Release Agent is a dispersion of hydrophilic polyester (polymer) with a functional polysiloxane. No further details from the SDS/TDS are available about the chemical content. It was easily biodegradable in the OECD 302B test. The product has been tested for acute toxicity in luminescent bacteria. The result was a $^{½h}EC_{50}$ > 5 g/L. In an acute fish toxicity test (OECD 203) with rainbow trout (*Oncorhynchus mykiss*) the $^{48h}LC_{50}$ was 1000 mg/L. Therefore, the acute toxicity of the product was low.

PHOBOTEX®WS CONC. **Hydrophobic Agent** is a non-ionic polysiloxane based emulsion. The product is classified as dangerous according to Directive 1999/45/EC and its amendments. It is harmful to aquatic organisms, and may cause long-term adverse effects in the aquatic environment. Besides the siloxane, the product contains 3-7% of the quaternary ammonium compound and emulsifier Cocoalkylbis(2-hydroxyethyl) ethoxylated methylammonium chloride/ *N,N*-Diethoxylated-*N*-coco-*N*-methylammonium chloride (CAS no. 61791-10-4), which is pre-registered in ECHA (ECHA, 2014c). According to the SDS, this chemical is classified as harmful for the environment (N, R51/53). The product was easily biodegradable (50-100%) in the OECD 303A test. The product has a low acute toxicity to bacteria with a $^{3h}IC_{50}$ >300 mg/L, but a higher toxicity to rainbow trout (*Oncorhynchus mykiss*) with a $^{48h}LC_{50}$ = 45 mg/L.

The Swedish OrganoTex® products (**OC-aquasil Tex W™, OC-aquasil Tex N™**) from OrganoClick mimicking nature (Lotus flower) contains <10.5% an unknown organic silicon compound and <5% of an organic acid. No information about their environmental properties is available.

RHODORSIL®TCS 7001 from Bluestar Silicones is an alkyl polysiloxane dispersion in a solvent phase (cyclohexane?) specifically developed for spray impregnation waterproofing. No environmental information is available. Classification has been done according to Directive 67/548/EEC with risk phrases: Harmful to aquatic organisms; may cause long-term adverse effects in the aquatic environment (R52/53).

4.4.2 Risk of releases of dangerous substances from treated textiles

The polymeric alternatives based on siloxanes for textile impregnation may contain and potentially release environmentally hazardous, very persistent and very bioaccumulative substances (vPvB) and substances evaluated to be persistent, bioaccumulative and toxic substances (PBT).

4.4.3 Overall environmental assessment of siloxanes

Detailed environmental assessment data for the cyclic and short-chain linear siloxanes are included in Appendix 2.

In a Nordic study, the occurrence of siloxanes (HMDSO, MDM, MD2M, MD3M, D3, D4, D5, and D6) in the Nordic environment (air, biota, sediment, sludge, soil, and water) was screened (Nordic Council of Ministers, 2005). Some factors relevant for the environmental assessment are taken from the Nordic report and shown in Table 6.

Siloxanes were found in all sample types except soil, and cyclic siloxanes occurred in all media in significantly higher concentrations than the linear siloxanes.

D5 was the dominating siloxane in all matrices except in air, where D4 dominated. Diffuse sources seem to be most important for the observed concentrations of siloxanes, and concentrations were generally elevated in urban areas and in areas close to STPs. Siloxanes were identified in fish livers, mainly from sites representing urban/diffuse sources, while only a few background samples showed detectable levels.

TABLE 6

THE OCTANOL-WATER PARTITION COEFFICIENT, BIOACCUMULATION FACTOR, HALF-LIFE IN AIR AND SOME ENVIRONMENTAL LEVELS FOR SOME SILOXANES FOUND IN THE AREA AROUND THE DANISH (COPENHAGEN) SEWAGE TREATMENT PLANT (STP) "LYNETTEN".

Substance	Log K_{ow}	BCF	Half-life in air, reaction with OH• (days)	Half-life in sediment (days)[a]	Waste water influent (µg/L)	Primary sludge (ng/g dw)	Waste water effluent (µg/L)	Fish from recipient area (ng/g ww)
D4	5.1[a]	12400; 1700[a]	16	38/340	0.28	740	<0.02	13.5
D5	5.2	5300;2000[a]	10	38/340	26	27000	0.063	52.3
D6					1.6	1100	<0.02	8.73
MM	4.2	900/340[a]	12	15/140	<0.01	<3	<0.02	<0.5
MDM	4.8	990[a]		38/340	0.0034	64	<0.02	<0.5
MD2M					0.041	450	<0.02	<0.5
MD3M	6				0.073	550	<0.02	<0.5

a) from Lassen et al. (2005).

Detailed ecotoxicity data from open literature was only obtained for D4 (see Table 7).

TABLE 7
ECOTOXICITY PARAMETERS FOR D4 (MODIFIED FROM NORDIC COUNCIL OF MINISTERS, 2005)

Organism	Endpoint	Adverse effect	Duration	Concentration (µg/L)
Opossum Shrimp (*Americamysis bahia*)	NOEC	Immobilisation	14 days	9.1
Midge (*Chironomus tentans*)	NOEC	Growth	14 days	> 15
Midge (*Chironomus tentans*)	NOEC	Mortality	14 days	>15
Sheepshead minnow (*Cyprinodon variegatus*)	NOEC	Mortality	14 days	6.3
Water flea (*Daphnia magna*)	NOEC	Immobilisation	48 hours	> 15
Water flea (*Daphnia magna*)	NOEC	Reproduction	21 days	1.7-15
Rainbow trout (*Oncorhynchus mykiss*)	LC_{50}	Mortality	14 days	8.5-13
Rainbow trout (*Oncorhynchus mykiss*)	LOEC	Mortality	14 days	6.9
Rainbow trout (*Oncorhynchus mykiss*)	NOEC	Mortality	14 days	≤ 4.4
Rainbow trout (*Oncorhynchus mykiss*)	NOEC	Multiple effects	93 days	4.4

Polydimethylsiloxanes (PDMS)
PDMS is an end-product, but it is pre-registered in REACH (ECHA, 2014c). It is notified in the C&L Inventory either as “not classified” or classified, among others, as Aquatic Chronic 2 and 4 (H411, H413) (ECHA, 2014d).

According to the producer Dow Corning, PDMS fluids pose no known hazard to the environment (Dow Corning, 1997). In the aquatic environment PDMS attaches to particulate matter and is removed from the water column by sedimentation. It is persistent and has no detectable Biological Oxygen Demand (BOD). In the soil PDMS may degrade abiotically in a few days to $(CH_3)_2Si(OH)_2$, a persistent metabolite. These organosilanols and low molecular weight linear PDMS and cyclic siloxanes may evaporate into the atmosphere. In the upper atmosphere they are oxidized by hydroxyl radicals to silica, water, and CO2 (Gravier et al. 2003).

4.5 Summary

Availability and technical properties - Many products are available and agents of this type have been on the market for many years. Various agents are available for different types of textiles. The agents provide durable water repellency but not oil repellency. For those products where the price indication is available, some are indicated as more expensive and other as less expensive than the PFAS-based agents.

Health assessment -. The most used silicones in textiles are polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH, and they are relatively inert and generally have no adverse effects. They are volatile and most exposures will occur by inhalation. Various other siloxanes, especially the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes HMDSO, MDM, MD2M and MD3M, may be used as intermediates for synthesis of silicone polymers used for textile impregnation. Specifically, D4 is suspected of damaging fertility, and D5 is a potential carcinogen.

The commercial product emulsions often contain other substances such as isotridecylalcohol, which is registered in REACH and is more harmful than the siloxanes. Some of the commercial products contain substances that are powerful irritants.

Environmental assessment - Siloxanes are relatively persistent and are widespread in the environment but are found mostly in urban areas and in the aquatic environment, including fish livers, close to STPs. They are removed from the aqueous phase by sedimentation, and have a long half-life there. In soils, depending on the conditions, siloxanes are transformed into hydroxylated forms, which may still be persistent.

PDMS has not been evaluated for lack of data. The bioconcentration factors and bioaccumulation factors for D4 are high, indicating D4 may have a high potential to accumulate in aquatic organisms, and according to an ECHA expert group, D4 met the criteria for a PBT and vPvB substance. D5 also met the criteria for a vPvB substance in the environment due to its persistence in sediment and a high bioconcentration factor in fish. D6, MM, MDM, MD2M, and MD3M were not considered a PBT or vPvB substance by the notifiers but the substance has not yet been evaluated by ECHA.

The commercial products contained substances other than siloxanes; some known, some unknown. Isotridecyl alcohol is less persistent but more toxic to aquatic organisms. A quaternary ammonium compound used was classified as harmful for the environment.

Main data gaps - There are sufficient health data to evaluate the cyclic and linear siloxanes. However, data are lacking concerning the actual silicon polymers used on the textiles.

Data indicating to what extent the siloxanes may be released during production of the textiles, use of the textiles and waste disposal have not been identified.

The environmental data on polydimethylsiloxanes are insufficient and environmental data on other possible silicone polymers used in textile products are lacking.

5. Dendrimer-based repellent chemistries

5.1 Chemistry

Dendrimer-based repellent chemistry is a relatively new field of repellent chemistry. The term merely gives indications about the physical structure, not about the chemical composition of the repellent. Dendrimers are repetitively branched molecules leading to monodisperse, tree-like structures. A hypothetical example is given in Figure 4 and further illustrated by the description of specific products below. The synthesis of monodisperse polymers demands a high level of synthetic control, which can only be achieved through step-by-step reaction, in which the dendrimer is built up by one monomer layer at a time. The primary components of each dendrimer are the core, internal cavities, branching units and closely packed surface groups (ZDHC, 2012).

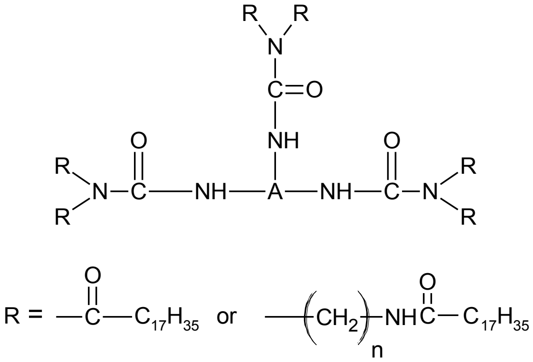


FIGURE 4
HYPOTHETICAL STRUCTURE OF A DENDRIMER SYNTHESIED FROM DISTERARYL-AMINES OR –AMIDES AND A TRIFUNCTIONAL ISOCYANATE (FROM SCHINDLER AND HAUSER, 2004).

Depending on the chemical composition, dendrimers can provide water and/or oil repellency. The company Rudolph Group, for example, offers different textile finish products based on dendrimer technology. The oil- and soil-repellent dendrimer finishes include a fluorocarbon resin in their structure, while the fluorocarbon-free dendrimers only provide water repellency. Compared to other PFAS-based repellents, the fluorine content of the oleophobic dendrimer finishes is reduced. The fluorocarbon-free dendrimers provide water repellency through closely packed surface groups, i.e. methyl groups.

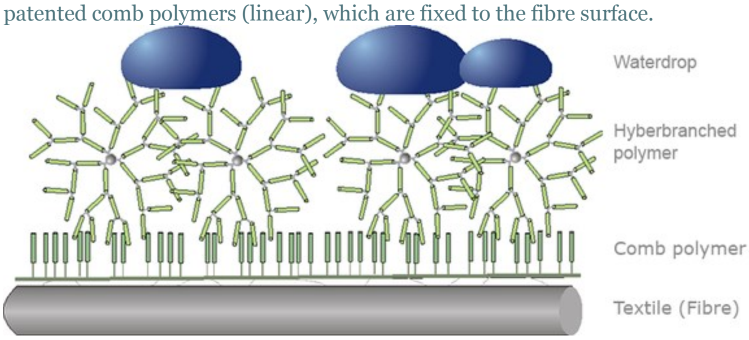
Commonly, these finishes are applied as two-component systems consisting of an emulsion containing the dendrimers and a solution containing a crosslinking substance providing the fixation to the fibre. Fluorocarbon-free dendrimers are based on hydrocarbon or polyurethane chemistry. Crosslinking is commonly achieved by chemical binding of the dendrimers with isocyanates to the fibre (Personal communication with the industry). Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers (UNEP, 2012 [Technical Paper]).

A number of products using this advanced technology are on the market. Regarding the innovation and research efforts, companies are investing in these products; it is typical that they do not disclose any chemical details on their products.

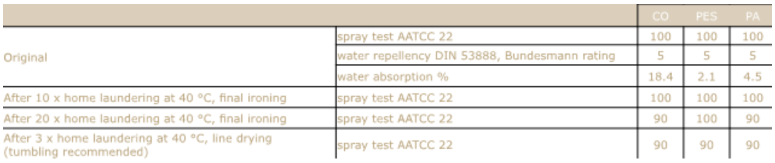
5.2 Examples of marketed products

The dendrimer-based repellents is a relatively new group of repellents on the market. According to a new Danish assessment of repellent finishing for children's clothes, many of the manufacturers have changed from PFAS-technology to non-fluorinated dendrimer-technology in recent years (Lassen et al., 2015).

Identified products from two manufacturers are listed below. The products Baygard WRC and Baygard WRS described as "3D" technology appear to apply a similar approach.

<table>
<tr><th colspan="2">Rudolf Group</th></tr>
<tr><td>Product name</td><td>®RUCO-DRY ECO (Brand BIONIC-FINISH® ECO)</td></tr>
<tr><td>Chemical properties</td><td>Polyurethane-dendrimer (hyperbranched polymers) with hydrophobic end groups connected to patented comb polymers (linear), which are fixed to the fibre surface.


Emulsion contains isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups-containing organopolysiloxane, and emulsifiers.</td></tr>
<tr><td>Functional properties</td><td>

Water-repellent, no oil-repellency
Better abrasion resistance than PFAS-based finishes
Not resistant to dry cleaning (in contrast to PFAS-based agents)
Soft handling (softer than fluorocarbon chemistry)
High gliding properties of the finished textile
Improves the sewability
Suitable for all fibre types
</td></tr>
<tr><td>Application areas</td><td>Clothing and non-clothing textiles made of cotton, polyester or blends.</td></tr>
<tr><td>Application process</td><td>No high curing temperatures necessary (recommended 150 °C for 2 min, 160 °C for 1 min or 170 °C for 30 s).</td></tr>
<tr><td>Wash resistance</td><td>High and comparable to C_6-fluorocarbon chemistry, but slightly worse than C_8-fluorocarbon chemistry.
Heat treatment above 65° C (tumbler "extra dry" or ironing) after each wash cycle to fully restore the effect level of the finish is recommended.

<table>
<tr><th></th><th></th><th>CO</th><th>PES</th><th>PA</th></tr>
<tr><td>Original</td><td>spray test AATCC 22</td><td>100</td><td>100</td><td>100</td></tr>
<tr><td></td><td>water repellency DIN 53888, Bundesmann rating</td><td>5</td><td>5</td><td>5</td></tr>
<tr><td></td><td>water absorption %</td><td>18.4</td><td>2.1</td><td>4.5</td></tr>
<tr><td>After 10 x home laundering at 40 °C, final ironing</td><td>spray test AATCC 22</td><td>100</td><td>100</td><td>100</td></tr>
<tr><td>After 20 x home laundering at 40 °C, final ironing</td><td>spray test AATCC 22</td><td>90</td><td>100</td><td>90</td></tr>
<tr><td>After 3 x home laundering at 40 °C, line drying (tumbling recommended)</td><td>spray test AATCC 22</td><td>90</td><td>90</td><td>90</td></tr>
</table></td></tr>
<tr><td>Price</td><td>"Competitive with fluorocarbon chemistry"</td></tr>
<tr><td>Information on release/emissions of the substance during use and/or wash</td><td>No data</td></tr>
<tr><td>Classification</td><td>The product is not required to be labelled according to Directive 1999/45/EC.</td></tr>
</table>

	Functionalized polymer (5-15%):Skin Irrit. 2, H315; Eye Irrit. 2, H319 Cationic surfactants (0.5-1%): Skin Corr. 1B, H314; Aquatic Acute 1, H400; Aquatic Chronic 2, H411; Acute Tox. 4, H302
Human health properties	Oral toxicity LD$_{50}$ (rat) > 5000 mg/kg
Environmental fate properties	Easily eliminated from the effluent (> 80% by OECD 302 B) Environmentally friendly – no durable decomposition products Bioaccumulation: no data Soil mobility: no data COD: 590 mg/g BI5: 110 mg/g
Environmental effects properties	Water toxicity: EC$_{50}$ (bacteria) > 100 mg/l, LC$_{50}$ (fish) > 100 mg/l) Further ecotoxicity tests are not available. Results of PBT and vPvB assessment: Not relevant.

<table>
<tr><th colspan="2">OrganoClick - OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)</th></tr>
<tr><td>Product name</td><td>OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)</td></tr>
<tr><td>Chemical properties</td><td>The water repellent effect is based on hydrocarbon chains. The product contains an organic silicon compound (<10.5%) and organic acid (<5%).
Composition of plant-based catalysts and organic polymers. The organic polymers have two different ends; one pointing outwards that is highly water repellent and one that is reactive that binds to the textile fibres. When the reactive end is unbound (before application to the textile) it is biodegradable. In the presence of the catalysts, the reactive end binds to the textile fibres and it is then rendered non-degradable and becomes highly durable instead.</td></tr>
<tr><td>Functional properties</td><td>• Water repelling
• Increased softness (compared to some fluorocarbons)
• Lower drying temperature (compared to some fluorocarbons)
• Durable protection against water, snow and water-based soiling such as stains from red wine, coffee, ketchup, etc.</td></tr>
<tr><td>Application areas</td><td>Woven and knitted textiles (W), nonwoven (felt-like) material containing either cellulose-based or synthetic fibres (N)</td></tr>
<tr><td>Application process</td><td>Pad-dry-cure process. Coating, spraying or padding with subsequent drying.</td></tr>
<tr><td>Wash resistance</td><td><table>
<tr><th></th><th>BEFORE HOME LAUNDRY</th><th>AFTER 20 HOME LAUNDRY CYCLES (ISO 6330)</th></tr>
<tr><td>Spray test (ISO 4920)</td><td>5 of 5</td><td>4 of 5</td></tr>
<tr><td>Spray test (AATCC 22)</td><td>100 of 100</td><td>90 of 100</td></tr>
</table></td></tr>
<tr><td>Price</td><td>More expensive (compared to some fluorocarbons)</td></tr>
<tr><td>Information on release/emissions of the substance during use and/or wash</td><td>No data.</td></tr>
<tr><td>Classification</td><td>This product is not classified as flammable, irritating or dangerous for the environment according to 1999/45/EC.
Organic silicon compound: Skin irrit. 2 (H315)
Organic acid: Skin irrit. 2, Eye irrit. 2, STOT SE 3 (H315, H319, H335)</td></tr>
</table>

OrganoClick - OC-aquasil Tex W™, OC-aquasil Tex N™ (brand name OrganoTex®)	
Human health properties	Information about the product is not available. Organic acid (in concentrated form) LD_{50} (mouse): > 1500 mg/kg Organic silicon compound (in concentrated form) LD_{50} (rat): > 5000 mg/kg Not classified as allergenic by inhalation or skin contact. The product does not contain any substances that are classified as carcinogenic, mutagenic or toxic for reproduction.
Environmental fate properties	The product is readily biodegradable according to OECD 301A/SS-EN ISO 7827:1996. Bioaccumulation-information about the product is not available. Organic acid (in conc. form): Log Kow: -1.26 Organic silicon compound (in conc. form): Is not regarded as being accumulative because it hydrolyses rapidly and will permanently bind to minerals, rendering it biologically unavailable. The product is soluble in water (soil mobility). The product is not considered to contain any substances that meet the criteria for classification as PBT or vPvB substances.
Environmental effects properties	Information about this preparation is not available. Organic silicon compound (in conc. form): LC_{50} (fish) > 1000 mg/L according to OECD 203, 96h LC_{50} (*Daphnia*) > 1000 mg/L according to OECD 202, 48h E_bC_{50}* (algae) > 30 mg/L according to OECD 201, 96h

* E_bC_{50} – effect concentration at which 50% reduction of biomass is observed

5.3 Health assessment

5.3.1 Health assessment on specific impregnation agents

RUCO-DRY ECO®: This dendrimer product is an emulsion containing isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups containing organopolysiloxane, and emulsifiers. According to the SDS, the product is not required to be labelled according to Directive 1999/45/EC. The product's oral rat LD_{50} > 5 g/kg bw. It may irritate airways when used in spray cans. The product contains 5-15% of an unknown functionalized polymer, which is skin- and eye irritating group 2 (H315 + H319), and 0.5-1% of an unknown cationic surfactant, which is harmful by intake (acute toxic group 4, H302) and corrosive to skin (H314). The content of a siloxane makes this product a hybrid between the substances discussed in sections 3.3 and 3.2, where siloxanes are discussed.

BIONIC-FINISH® ECO is a hyperbranched/linear and cationic polymer, highly effective water-repellent agent for finishing fabrics of all fibre types, when combined with crosslinking boosters, such as RUCO-LINK RCX, RUCO-LINK DAL, RUCO-LINK BEW or RUCO-LINK EIT.
In the material from the producer there was no information on properties relevant for health.

OC-aquasil™ Tex W, according to the producer, is not classified as dangerous for the environment according to Directive 1999/45/EC. Information about the exact composition of the product is not available; however, it contains <10.5% of an unknown organic silicon compound, which is skin-irritating and has a low acute toxicity in rats (LD_{50} >5 g/kg bw). Hazard statement: H315: Causes skin irritation. The content of a siloxane makes this product a hybrid between the substances discussed in sections 3.3 and 3.2, where siloxanes are discussed. In addition, the product contains <5% of an unknown classified organic acid which irritates both skin and eyes and has a specific target organ toxicity after a single exposure (STOT SE 3). Its oral LD_{50} in mice is >1500 mg/kg bw. Hazard statements H315, H319: Causes serious eye irritation, and H335: May cause respiratory irritation.

The most important symptoms mentioned in the SDS were:

Inhalation:	May cause drowsiness, nausea, dizziness and light-headedness
Skin contact:	May cause skin irritation such as redness and pain
Eye contact:	May be irritating to the eyes causing pain, redness and tearing
Ingestion:	May cause nausea, pain, dizziness and breathing disorders.

This product and its ingredients seem to be more hazardous than the producer indicates, and without information about the exact chemicals and concentrations, it is impossible to clear this product as regards concern for health.

5.3.2 Risk of dangerous substances in the treated textile

No information but there may be residues of isocyanates and siloxanes.

5.3.3 Risk of formation of dangerous substances by degradation of cured repellents

No information but isocyanates and siloxanes may be formed and released by evaporation.

5.4 Environmental assessment

5.4.1 Environmental data on specific impregnation agents

RUCO-DRY®ECO from Rudolf Group is a dendrimer product formulated as an emulsion containing isocyanates as cross-linking agents, C_8-C_{18}-alkyl groups-containing organopolysiloxane, and emulsifiers. The product contains 5-15% of an unknown functionalized polymer, and 0.5-1% of an unknown cationic surfactant. The content of a siloxane makes this product a hybrid between the substances discussed sections 3.3 and 3.2. According to the SDS, the product is not required to be labelled according to Directive 1999/45/EC. The product was easily biodegradable (>80%) in the OECD 302B test. The product has not been tested for ecotoxicity but, by read across, the acute ecotoxicity for fish was estimated to LC_{50} >59 mg/L, and the EC_{50} for sewage sludge bacteria was >100 mg/L. The risk phrases H400: “Very toxic for aquatic organisms”, and H411: “Toxic for aquatic organism; with long-term effects” is indicated in the MSDS.

BIONIC-FINISH®ECO from Rudolf Group is a hyperbranched/linear and cationic polymer, highly effective water-repellent agent, when combined with crosslinking boosters such as RUCO-LINK RCX, RUCO-LINK DAL, RUCO-LINK BEW or RUCO-LINK EIT. In the material from the producer there was no information on product composition or environmental properties.

OC-aquasil™ Tex W, according to the SDS from OrganoClick, is not classified as dangerous for the environment according to Directive 1999/45/EC. Information about the exact composition of the product is not available; however, it contains <10.5% of an unknown organic silicon compound, that makes this product a hybrid between the substances discussed sections 3.3 and 3.2. In addition, the product contains <5% of an unknown organic acid. The product is soluble in water and readily biodegradable according to OECD 301A. Neither the organic acid ($LogK_{ow}$ = -1.26) nor the silicon compound were assessed to be bioaccumulative. The silicon compound has been tested for ecotoxicity with the following results: $^{96h}LC_{50}$ (fish) > 1000 mg/L according to OECD 203, $^{48h}LC_{50}$ (*Daphnia*) > 1000 mg/L according to OECD 202, and $^{96h}EC_{50}$ (algae) > 30 mg/L according to OECD 201.

5.4.2 Risk of dangerous substances in the treated textile

No information but there may be residues of isocyanates and siloxanes.

5.4.3 Risk of formation of dangerous substances by degradation of cured repellents

No information but isocyanates and siloxanes may be formed and released by evaporation.

5.5 Summary

Availability and technical properties - The agents of this type are relatively new. Few types have been identified. Application areas cover various clothing and non-clothing textiles. The agents are currently widely used for children's clothing on the Danish market. The agents provide durable water repellency but not oil repellency. The prices range from comparable to the PFAS-based agents to more expensive.

Health assessment - There are no data available on health properties of these unknown active substances and other components, but the producers of commercial products have included a few health data in the MSDS's and made some proposals for classification of the product. According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently, but some of the products contain unknown siloxanes likely discussed above, cationic polymers, isocyanates or powerful irritating organic acids. In general, relevant information for health assessment for this group of chemicals is insufficient. Therefore, it is not possible to assess the possible health effects of the agents.

Environmental assessment - The product compositions of these repellents were not specified sufficiently but some of the products contain unknown siloxanes, cationic polymers, isocyanates or powerful irritating organic acids. According to the producer's information, these products should not be labelled or classified as harmful for the environment, but it is not possible on the basis of the available information to evaluate these statements.

Main data gaps - In general, the relevant information for health and environmental assessment of this group of products with unknown ingredients is insufficient.

6. Polyurethane repellent chemistries

6.1 Chemistry

The polyurethane-based repellents represent a relatively new group of repellents. They are briefly mentioned in the report from ZDHC (2012), but not described in detail. They are not described by Schindler and Hauser (2004). Aside from the polyurethane polymer matrix, the repellent effect is caused by the covalent implementation of hydrophobic copolymers based on silicones and/or paraffins, and the product may alternatively have been grouped with the paraffin-based or silicone-based repellents.

The chemistry is described for one product in the next section with examples of marketed products. The manufactured fabric is breathable and the impregnation agent is therefore different from waterproof fabric coated with polyurethane used e.g. for raincoats.

6.2 Examples of marketed products

The polyurethane-based repellents represent a relatively new group of repellents on the market. One product has been identified and is listed below.

Freudenberg Group	
Product name	Purtex® WR water repellent
Chemical properties	Water-based, aliphatic polyurethane emulsion, two-component system Component A: Emulsion with polyurethane content of 70% Component B: Crosslinker containing blocked isocyanates The durable water repellent effect is caused by the covalent implementation of hydrophobic copolymers based on silicones and/or paraffins which also exert a positive influence on the softness of the finished textile.
Functional properties	• Durable water repellent, no oil-repellency • Good abrasion resistance (abrasion resistance of the fibre improved) • Heat treatment after wash to fully restore the effect level of the finish not necessary (Laundry air dry, LAD). • Soft handling (cotton becomes softer, polyester becomes more stiff) • Good ageing properties (light fastness) • Categorised as “extremely breathable” by external test institute
Application areas	Clothing and non-clothing textiles, suitable for most textiles
Application process	Usual wet finishing machine. Curing temperature 120-150°C. Component A can be diluted with water.
Wash resistance	Basically unchanged water repellency after 20 cycles of domestic laundering according to Bundesmann rain-shower test.

Price	Possibly comparable to PFAS-based products (depending on quality of the PFAS-based product, functional requirements and application)
Information on release/emissions of the substance during use and/or wash	Good hydrolysis resistance VOC and solvent free No isocyanate or VOC emissions as tested by headspace and extraction GC/MS
Classification	Product not classified according to EC regulation 1272/2008 (CLP).
Human health properties	Prepolymer: Oral toxicity LD_{50} (rat) > 5000 mg/kg (OECD 423) Mutagenicity: negative (Escherichia coli – OECD 471), negative (Salmonella typhimurium – OECD 471)
Environmental fate properties	No data on PBT or vPvB properties of the product. Prepolymer: Persistence in the environment possible. BCF < 500 (EpiWin calculated) Log Kow > 3 (EpiWin calculated) Log Koc > 3 (EpiWin calculated) No further data on PBT or vPvB properties.
Environmental effects properties	Prepolymer: NOEC (*Daphnia magna*) 100 mg/L (OECD 202) LOEC (*Daphnia magna*) >100 mg/L (OECD 202) EC_{50} (*Daphnia magna*) >100 mg/L (OECD 202) EC_{100} (*Daphnia magna*) >100 mg/L (OECD 202)

6.3 Health assessment

6.3.1 Health data on specific impregnation agents

There is no available health data on the ingredients in **Purtex® WR 6110**, a two-component water-based, aliphatic polyurethane emulsion system with a crosslinker containing blocked isocyanates.

The product and both components are considered not hazardous as per the EU Dangerous Substances Directives by the producer. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS:

- P280: Wear protective gloves/protective clothing/eye protection/face protection.
- P311: Call a POISON CENTER or doctor/physician.
- P333/313: If skin irritation or rash occurs: Get medical advice/attention.

Furthermore, it is mentioned that inhalation of gases, vapours and aerosols and exposure to skin and eyes should be avoided. In addition, it is mentioned that heating may release harmful vapours. The toxicity tests applied on a prepolymer (unclear if it is component A or B) was an oral rat LD_{50} of > 5 g/kg bw; therefore, this component had no acute toxicity, and two tests for mutagenicity in bacteria were also negative but no details were given. Without the name and CAS no. of the isocyanates, the claims of the producer are impossible to verify.

However, organic isocyanates are generally highly irritating, allergic and toxic. For instance, methyl isocyanate is known as the Bhopal toxin. PUR may also contain residues/impurities of unreacted highly toxic isocyanates or aromatic amines.

6.3.2 Risk of dangerous substances in the treated textile

Residues of unreacted toxic isocyanates may be found.

6.3.3 Risk of formation of dangerous substances by degradation of cured repellents

It is stated that no evaporation of VOC and isocyanates takes place.

6.4 Environmental assessment

6.4.1 Environmental data on specific impregnation agents

Purtex®WR 6110 from Freudenberg is a two-component water-based, aliphatic polyurethane emulsion system with a crosslinker containing blocked isocyanates. No information about the substance composition is provided. The product and both the components are considered not environmentally hazardous as per the EU Dangerous Substances Directives (67-Directive and CLP) by the MSDS. The prepolymer has been tested according to OECD 202, and both the NOEC and LOEL in *Daphnia magna* was 100 mg/L. The BCF and log K_{ow} for the prepolymer has been calculated to be <500 and >3, respectively. There is no available environmental data on the other ingredient.

6.4.2 Risk of releases of dangerous substances from treated textiles

It is stated in the SDS that no evaporation of VOC and isocyanates take place.

6.5 Summary

Availability and technical properties - The agents of this type are relatively new. Only one type has been identified. This type of agent is suitable for most textiles. The agent provides durable water repellency but not oil repellency. Price information for one product indicated that the price is likely comparable to PFAS-based products.

Health assessment - Only one commercial product is identified. Its composition is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS. Generally, the content of organic isocyanates makes the product potentially hazardous to skin and mucous membranes. Therefore, it is not possible to assess the possible health effects of the agents in detail.

Environmental assessment - The composition of the product is not detailed, either qualitatively or quantitatively. According to the producer's information, the product should not be labelled or classified as harmful to the environment. However, due to lack of relevant data, it is not possible to verify these claims.

Main data gaps - This product group shows a lack of public health and environmental data and insufficient information about product composition as well as the substances formed at the impregnation process.

7. Other

Various water repellents based on other chemistries are on the market. Table 1 lists a few repellent product details. Information was not available on how stain repellency was achieved; this information has also not been available from the manufacturer's websites. This information concerns Arristan HPC from CHT/Bezema, H2O Repel from Devan (the product may have been discontinued) and Careguard FF from Sarex. Information on a few other identified agents/types is provided below.

7.1 NEOSEED

7.1.1 Marketed products

NEOSEED from Nicca Chemical Co. is a water repellent based on a non-ionic unknown polymer and unknown ingredients (see Table below).

NICCA CHEMICAL CO.,LTD.	
Product name	NEOSEED NR-90
Chemical properties	Non-ionic Polymer, Ester Compound, Hydrocarbon compound, Organic Solvent and Water
Functional properties	• Water repellency • No oil repellency • Hand is a little stiffer than PFAS-based products
Application areas	Clothing and non-clothing textiles (polyester, nylon, cotton, all kind of fabric) carpet ・table cloth ・wallpaper ・umbrella ・suit, coat ・surgical gown ・uniform ・automotive engine filter ・outdoor garments ・cardboard
Application process	Standard application: 2 to 6 % solution by pad application.
Wash resistance	No data
Price	About the same range as current PFAS-based water repellent (C_6)
Information on release/emissions of the substance during use and/or wash	No data
Classification	No data
Human health proper-	No data

ties	
Environmental fate properties	BOD_5 41 ppm (0.1%) COD (Mn) 115 ppm (0.1%)
Environmental effects properties	LC_{50} (Red killifish, 96 h) 250 ppm

7.1.2 Health assessment

Health data on specific impregnation agents

NEOSEED NR-90 is a white liquid offering water repellence. Its composition is only general and qualitatively known as a non-ionic polymer, with ester and hydrocarbon compounds. The active repellent ingredient is not identified. It is claimed that: "No reportable quantities of hazardous ingredients are present." No documentation for the claim is found, and no test results are given for toxicity, irritation, mutagenicity etc.

However, it is mentioned under Hazard Identification that the product:

- "May be irritating to eyes"
- "Prolonged or repeated contact may cause skin irritation"
- "May be harmful if swallowed".

In addition, some first-aid measures (precaution phrases) are mentioned, indicating that the product is not without health hazards. It is not possible to verify the producers' claim of a non-hazardous product.

Harmonised classification

None.

Risk of dangerous substances in the treated textile

No information is available.

7.1.3 Environmental assessment

Environmental data on specific impregnation agents

NEOSEED NR-90 from NICCA is a white water-soluble liquid offering water repellence. Its composition is only generally and qualitatively known as a non-ionic polymer, with ester and hydrocarbon compounds. The active repellent ingredient is not identified either. It is claimed that: "No reportable quantities of hazardous ingredients are present." The $^{96h}LC_{50}$ in red killifish (*Aphyosemion bivitattum*) was 250 ppm.

Harmonised classification

None.

Risk of dangerous substances in the treated textile

No information is available.

7.1.4 Summary

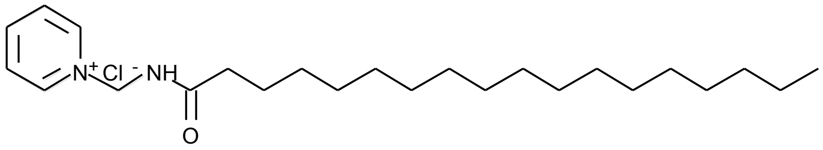
Availability and technical properties - The agents of this type are relatively new. Few types have been identified. Application areas cover various clothing and non-clothing textiles. The agents provide durable water repellency but not oil repellency. Price information for one product indicated that the price is comparable to PFAS-based products.

Health assessment - For one commercial product, described as a non-ionic polymer with ester and hydrocarbon compounds, it was claimed that: "No reportable quantities of hazardous ingredients are present." However, no documentation for that claim as regards health effects was given, and some risk phrases were mentioned, indicating skin- and eye-irritating properties and harmfulness if swallowed. Therefore, it was not possible to verify the producers' claim of a non-hazardous product.

Main data gaps - Documentation for the non-hazardous claim is lacking.
Environmental assessment - For one commercial product, described as a non-ionic polymer with ester and hydrocarbon compounds, it was claimed that: "No reportable quantities of hazardous ingredients are present."

7.2 Stearamidomethyl pyridinium chloride

A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, which was previously marketed by ICI as Velan PF:



This substance can react with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibres and that the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction had an unpleasant odour, and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s, when government regulation of such substances increased; however, it appears that it still is used in mixture with siloxanes (see above).

The health and environmental data are insufficient for an assessment.

7.3 Nanomaterial-based repellent chemistries

Repellent chemistries containing nano-materials are coated on fabrics to achieve desirable properties without a significant increase in weight, thickness or stiffness. As is the case with the dendrimer technology, the term "nanomaterials" does not disclose any information on chemical composition. According to a research report on water repellent (ZDHC, 2012), the use of nanomaterials to impart water repellency and stain resistance effects on textile is one of the most common ways nanotechnology is being used in the textile industry. These attributes are achieved by embedding fabrics with tiny fibres, called nano-whiskers, which form a cushion of air around fibre to repel water and stains. The treatment is believed to be durable to repeated home laundering cycles.

During the market research for this survey, no nanomaterial-based repellent products refraining from the use of fluorine technology were identified. A few companies (Schoeller, BASF, Nanotex) market products containing nanoparticles which are surface-treated with fluorine chemistries. In fact, the products actually form fluooroalkyl polymers at the surface. Further details on these chemistries have consequently not been obtained.

8. Conclusion

The obtained information on the alternatives is summarised in the following table.

It can be concluded that no alternatives matching the PFAS-based repellents on all technical parameters are available. The alternatives provide durable water repellency, but no repellency against oil, oil-based dirt and alcohol.

Regarding health and the environment, for most of the alternative impregnation agents reviewed, there is insufficient qualitative and quantitative public information about the ingredients. Only a few specific ingredients are stated and for these, limited data on health and environmental properties are available. The summary in the table is thus based on the limited information available.

According to the producer's information, most of the products should not be labelled or classified as harmful to the environment, but on the basis of the available information, for many products it is not possible to verify these statements. Apart from the siloxanes, where it is unclear which cyclic or small linear siloxanes are present in the products, the agents do not appear to contain significant amounts of persistent substances.

Furthermore, very little information on trace levels of raw materials, intermediates and substances formed by decomposition in the final products is available.

TABLE 8
SUMMARY OF TECHNICAL MAIN TECHNICAL PROPERTIES REGARDING REPELLENCY, AVAILABILITY PRICE, HEALTH PROPERTIES AND ENVIRONMENTAL PROPERTIES.

Type	Technical properties	Availability; price *	Health properties of impregnation agents *	Environmental properties of impregnation agents **
Paraffin-based repellents	Durable water repellent - no oil and alcohol repellency	Many products on the market. The agents are cheaper compared to the PFAS-based, but requires a higher dosage	The main ingredient in most products is paraffin oil/wax, i.e. mixtures of long chain alkanes (linear aliphatic hydrocarbons), which is harmless in its pure form. The compositions of the products are mainly confidential, but some products also contain isocyanates, dipropylene glycol, metal salts or other unspecified substances, which may be harmful.	Most components are readily biodegradable, are not bioconcentrated or accumulated in organisms and food chains, and aquatic toxicity is insignificant

Type	Technical properties	Availability; price *	Health properties of impregnation agents *	Environmental properties of impregnation agents **
Silicone-based repellents	Durable water repellent - no oil and alcohol repellency	Many products on the market. Price approximately the same as PFAs-based	The silicones most used in textile impregnation agents are based on polydimethylsiloxanes (PDMS). These siloxanes are registered in REACH, they are inert and generally have no adverse effects. Unclear to what extent cyclic and small linear siloxanes may be present at trace levels in the agents. Specifically D4 is suspected of damaging fertility, and D5 is a potential carcinogen.	Not enough data for a detailed evaluation. Unclear which siloxanes may be present at trace levels in the agents. Some cyclic siloxanes are PBTs. Low-molecular-weight poly(dimethylsiloxanes) and polydimethylsiloxanes (PDMS) have low toxicity and are not considered PBT or vPvB substances.
Dendrimer-based repellents	Durable water repellent - no oil and alcohol repellency	Few products identified. Price range from approximately the same as PFAS-based to slightly more	According to the producer's information, these products should not be labelled or classified as harmful. The product compositions were not specified sufficiently for an assessment, but some of the products contain unknown siloxanes (likely among those discussed above), cationic polymers, isocyanates or powerful irritating organic acids.	Not enough data for a detailed evaluation. According to the producer's information, these products should not be labelled or classified as harmful for the environment.
Polyurethane-based repellents	Durable water repellent - no oil and alcohol repellency	One product identified. Price approximately the same as PFAS-based to slightly more	According to the producer's information, the product should not be labelled or classified as harmful to health. Nevertheless, several health hazard precaution phrases are mentioned in the MSDS.	Not enough data for a detailed evaluation. According to the producer's information, these products should not be labelled or classified as harmful for the environment.
Other repellents	Durable water repellent - no oil and alcohol repellency	Few products identified. Price approximately the same as PFAS-based	It is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients". However, no documentation for this was provided, and some risk phrases were mentioned for the product indicating skin- and eye irritating properties and harmfulness if swallowed.	Not enough data for a detailed evaluation. For one commercial product it is indicated by the manufacturer that the product include "no reportable quantities of hazardous ingredients

* Price comparison is approximate as the price of PFAS-based repellents and the alternatives vary between specific repellents and also by specific applications.

** Concerns the substances in the agents and not trace levels of raw materials or degradation products.

Abbreviations and acronyms

3D	Three-dimensional
AATCC	American Association of Textile Chemists and Colorists
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
BOD/BI5	Biochemical Oxygen Demand
BSI	Bundesverband der Deutschen Sportartikel-Industrie e.V.
Bw	body weight
CEFIC	European Chemical Industry Council
CHO	Chinese Hamster Ovary
CIR	Cosmetic Ingredient Review
CLP	Classification, Labelling and Packaging (Regulation(EC) No 1272/2008)
CNS	Central Nervous System
COD	Chemical Oxygen Demand
C&L	Classification and Labelling (Inventory under REACH)
D3	Cyclotrisiloxane
D4	Cyclotetrasiloxane
D5	Cyclopentasiloxane
D6	Cyclohexasiloxane
D7	Cycloheptasiloxane
DIN	Deutsches Institut für Normung (German Institute for Standardisation)
DNA	Deoxyribonucleic acid
DNEL	Derived No Effect Level
DOC	Dissolved Organic Carbon
Dw	dry weight
DWR	Durable Water Repellent
E_bC_{50}	Effect concentration at which 50% reduction of biomass is observed
EC	European Commission
EC_n	Effect concentration where n % of the species tested show the effect
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
EOG	European Outdoor Group
EPA	Environmental Protection Agency
EU	European Union
GC/MS	Gas Chromatography/Mass Spectrometry
GLP	Good Laboratory Practice
HMDSO	Hexamethyldisiloxane (elsewhere also abbreviated MM or HMDS)
IC	Inhibition Concentration
ICR	Imprinting Control Region
INCI	International Nomenclature of Cosmetic Ingredients
ISO	International Organization for Standardization
Koc	Organic carbon/water partitioning coefficient
Kow	Octanol/water partitioning coefficient
LAD	Laundry Air Dry
LC	Lethal Effect Concentration
LD	Lethal Effect Dose

LOAEL	Lowest Observable Adverse Effect Level
LOUS	List of Undesirable Substances (of the Danish EPA)
MDM	Octamethyl trisiloxane
MD2M	Decamethyl tetrasiloxane
MD3M	Dodecamethyl pentasiloxane
MM	Hexamethyldisiloxane
MSDS	Material Safety Data Sheet
NOAEC	No Observable Adverse Effect Concentration
NOAEL	No Observable Adverse Effect Level
NOEC	No Observable Effect Concentration
NOEL	No Observable Effect Level
OECD	Organisation for Economic Co-operation and Development
OIA	Outdoor Industry Association
OPPTS	Office of Prevention, Pesticides and Toxic Substance
PBT	Persistent, Bioaccumulative and Toxic (in the environment)
PDMS	Polydimethylsiloxanes
PFAS	Entire group of perfluoroalkyl and polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonic Acid
PNEC	Predicted No Effect Concentration
POPs	Persistent Organic Pollutants
ppm	parts per million
PU/PUR	Polyurethane
PVC	Polyvinylchloride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation)
SCCP	The Scientific Committee on Consumer Products
SDS	Safety Data Sheet
STP	Sewage Treatment Plant
TDS	Technical Data Sheet
TOC	Total Organic Carbon
UNEP	United Nations Environment Programme
VOC	Volatile Organic Compound
vPvB	Very Persistent and very Bioaccumulative
ww	Wet weight
ZDHC	Zero Discharge of Hazardous Chemicals (concerted action)

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Appendix 1: Health data on selected siloxanes in registration dossiers

The following information has been extracted from the REACH registration dossiers available from ECHA's Dissemination Site Database (ECHA 2014, b).

Octamethylcyclotetrasiloxane (D4) is registered under REACH (ECHA, 2014e). From the REACH dossier, the following information can be extracted:

- D4 was readily >75% absorbed orally in rats when dissolved in corn oil and diet. Most was excreted shortly again in exhaled air or in the urine as polar metabolites.
- In an *in vitro* study with human skin the dermal absorption was 8.2% of the D4 substance.
- About 5 % of D4 inhalation exposure was absorbed in the lungs after 6 hours' exposure.
- In male rats the acute oral LD_{50} was >4.8 g/kg bw.
- An acute inhalation $^{4h}LC_{50}$ value of >36 mg/L (2975 ppm) air was determined in rats.
- The acute dermal toxicity was low with a LD_{50} value of >2500 ml/kg (>2400 mg/kg bw).
- D4 was not skin irritating for rabbits in an acute dermal irritation test (OECD 404). D4 was neither eye irritating nor skin sensitizing in the guinea-pig maximisation test (OECD 406).
- In a two-week repeated dose oral toxicity study the NOAEL for D4 was < 500 mg/kg bw/day in rabbits.
- Inhalation exposure to D4 for up to 24 months induced the following notable effects in male and female rats:
    - Reduced two-year survival and terminal body weight of male rats exposed to 700 ppm.
    - Lymphocytic leukocytosis in both sexes of rats exposed to 700 ppm.
    - A dose-related decrease in selected serum enzymes in both sexes of rats.
    - Increases in absolute and/or relative weight of liver, kidney, and uterus of D4-exposed rats, especially at 700 ppm.
    - Increased incidence of rhinitis in males exposed to 700 ppm for 12 months.
    - Increased incidence and severity of changes in the nasal epithelium of both sexes of rats exposed to 700 ppm and females exposed to 150 ppm for 24 months.
    - Increased severity of chronic nephropathy in both sexes of rats exposed to 700 ppm for 24 months.
    - Increased incidence of hypertrophy of hepatocytes in male rats exposed to 700 ppm for 12 or 24 months.
    - Increased incidence of endometrial adenomas and endometrial epithelial hyperplasia in the uteri of rats exposed to 700 ppm for 24 months.
    - The NOAELs for carcinogenic effects were 150 and ≥700 ppm in females and males, respectively. The NOAEL for general toxicity was 150 ppm, based on chronic nephropathy. The NOAEL for local respiratory effects was also 150 ppm based on findings in the nasal cavity.
- In a three-week dermal exposure study in rabbits (OECD 410) the dermal NOAEL was greater than the highest dose tested: 1 ml/kg bw/day.
- D4 was not inducing chromosome aberrations in Chinese Hamster Ovary (CHO) cells *in vitro* (OECD 473).
- D4 was not mutagenic in mouse lymphoma L5178Y cells or in Ames test with *Salmonella typhimurium* or in other *in vitro* tests.
- D4 was also negative in *in vivo* studies such as the micronucleus assay and dominant lethal assay.

DNELs have been developed:

- For workers via inhalation the DNEL for systemic and local effects was estimated to 73 mg/m^3 based on a NOAEC = 915 mg/m^3 and an assessment factor of 12.5.
- For workers and the general population no hazard via dermal route or for the eye identified.
- For the general population via inhalation the DNEL for systemic effects was estimated to 13 mg/m^3 based on a NOAEC = 325 mg/m^3 and an assessment factor of 25.
- For the general population via oral route the DNEL for systemic effects was estimated to 3.7 mg/kg bw/day based on a NOAEL = 374 mg/kg bw/day and an assessment factor of 100.

Decamethylcyclopentasiloxane (D5) is registered under REACH. Data submitted show that in an inhalation toxicokinetics study with rats approximately 2% of the inhaled ^{14}C-labeled D5 was retained regardless of sex or exposure concentration. D5 was excreted in urine (metabolites: dimethylsilanediol and methylsilanetriol) and faeces (parent D5) in approximately equal proportions. The skin absorption in rats was also very low at <1.2%; in human skin *in vitro* even lower, at 0.04%. Approximately 20% of ^{14}C-D5 delivered in corn oil appeared to be absorbed after a single oral administration in rats. Oral rat LD_{50} was > 5 g/kg bw, thus no acute toxicity. In rats the inhalation $^{4h}LC_{50}$ was 8.67 mg/L air or >545 ppm (6.72 mg/L). The dermal LD_{50} in rats and rabbits was > 2 g/kg bw. D5 was not skin irritating in rats and rabbits, eye irritating in rabbits or skin sensitising in guinea-pigs.

In a repeated dose 90-day oral toxicity study with rats (OECD 408), the NOAEL of D5 was considered to be greater than or equal to the highest dose tested, 1000 mg/kg bw/day. In a two-year inhalation combined chronic toxicity and carcinogenicity study with rats, the NOAEC for general toxicity was ≥160 ppm (2.42 mg/L; the highest dose tested). Local effects on the nasal cavity and adaptive increases in liver weights in females were observed at 160 ppm. The NOAEC for carcinogenic effects was 40 ppm (0.6 mg/L) based on uterine tumours at 160 ppm. D5 was negative in *in vitro* mutagenicity tests with bacteria, mouse lymphoma cells, and Chinese hamster lung fibroblasts. *In vivo* there was no induction of unscheduled DNA synthesis in the hepatocytes of treated rats, and no observation of increased levels of micronuclei in the bone marrow cells of the treated rats.

In a two-generation reproductive toxicity study no parental toxicity in the F0 and F1 generations was observed at air exposure concentrations of 30, 70, and 160 ppm. The NOAEL was determined to be > 160 ppm. D5 was an inhibitor of human and rat cytochrome P450 enzymes.
DNELs have been developed:

- For workers via inhalation the DNEL for systemic effects was estimated to 97.3 mg/m^3 based on a NOAEC = 1216 mg/m^3 and an assessment factor of 12.5.
- For workers via inhalation the DNEL for local effects was estimated at 24.2 mg/m^3 based on a NOAEC = 1216 mg/m^3 and an assessment factor of 12.5.
- For the general population via inhalation the DNEL for systemic effects was estimated at 17.3 mg/m^3 based on a NOAEC = 432 mg/m^3 and an assessment factor of 25.
- For the general population via inhalation the DNEL for local effects was estimated at 4.3 mg/m^3 based on a NOAEC = 432 mg/m^3 and an assessment factor of 25.
- For the general population via oral route the DNEL for systemic effects was estimated at 5 mg/kg bw/day based on a NOAEL = 1000 mg/kg bw/day and an assessment factor of 200.
- No hazards to skin and eyes were foreseen.

Dodecamethylcyclohexasiloxane (D6) is registered in REACH (ECHA, 2014g). From the dossier, the following information can be extracted:

- In a toxicokinetic study a single oral dose of labelled D6 (1000 mg/kg bw/day) given to male and female rats was largely excreted as D6 in the faeces within 48 h, with less than 12% having been absorbed. Radioactivity recovered in the urine (0.3-0.4% of the adminis-

tered dose) was present exclusively as polar metabolites; two major metabolites, methylsilanetriol (50-70%) and dimethylsilanediol (30-50%), were identified. Low levels of radioactivity were detected in organs and tissues (liver, fat, bone marrow), and small amounts of metabolites were present in the blood.
- An *in vitro* study (OECD 428) found virtually no penetration (0.003%) by D6 through samples of human skin in 24-h semi-occluded contact. Most of the substance evaporated.
- The oral (gavage) LD_{50} for acute toxicity (OECD 423) in female rats has been determined at >2 g/kg bw.
- An acute dermal single application LD_{50} value of >2000 mg/kg was determined for male and female rats in a study according to OECD Guideline 402.
- The substance was not skin irritating in a study (OECD 404) with rabbits or eye irritating in rabbits (OECD 405).
- D6 was not causing skin sensitisation in the guinea-pig maximisation test.
- In an oral combined repeated dose/reproductive and developmental toxicity study in the rat (OECD 422) the NOAEL for systemic toxicity of D6 via the oral route was determined to be 1000 mg/kg/day (highest dose tested).
- In a 90-days inhalation study with rats, hyperplasia and inflammation in the nasal tissue were observed at 10 and 30 ppm but not at 1 ppm. Thus the NOAEL was 1 ppm (182 mg/m^3) and the lowest observable adverse effect level (LOAEL) was 10 ppm (182 mg/m^3).
- D6 was not mutagenic in *in vitro* bacteria tests (OECD471) with *Salmonella typhimurium* strains TA1535, TA1537, TA100 and TA98 (Ames test) and *Escherichia coli WP2uvrA*.
- In an *in vivo* micronucleus assay in ICR mice (OECD474) no increases in micronucleated polychromatic erythrocytes was observed.

DNELs have been developed for D6:
- For workers via inhalation the DNEL for systemic effects was estimated at 11 mg/m^3 based on a NOAEC = 274 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects was 1.22 m/m^3 based on a LOAEC = 10 ppm = 182 mg/m^3 and an assessment factor of 75.
- For workers no hazard via dermal route was identified.
- For the general population via inhalation the DNEL for systemic effects was estimated to 2.7 mg/m^3 based on a NOAEC = 137 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects was 0.3 mg/m^3 NOAEC = 18.2 mg/m^3 and an assessment factor of 75.
- For the general population via dermal route no hazard was identified.
- For the general population via oral route the DNEL for systemic effects was estimated to 1.7 mg/kg bw/day based on a NOAEL = 1000 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were identified.

Hexamethyldisiloxane (HMDSO) is registered under REACH (ECHA, 2014h). From the dossier, the following information can be extracted: (the acronym HMDS is used)
- In an *in vivo* toxicokinetics study with rats exposed nose-only for 14 days (OECD 417). The majority of systemically absorbed HMDS (MM?) was eliminated in the urine as polar metabolites during 24 hours or was expired. Of the about 3% retained most was found in fat, kidneys and ovaries.
- In an in vitro dermal absorption 24-h study only 0.023% of the applied dose of hexamethyldisiloxane was absorbed through human cadaver skin. The majority of the dose volatilised from the application site (97.5%).
- The acute oral (gavage) rat LD_{50} (OECD 401) was determined to be > 3200 mg/kg bw,
- An acute inhalation $^{4h}LC_{50}$ of 15,956 ppm (equivalent ca. 106 mg/l) was determined in a study according to OECD Guideline 403.

- An acute dermal single application LD_{50} value of >2000 mg/kg was determined for male and female rats in a study according to OECD Guideline 402.
- The substance was not skin irritating in a study (OECD 404) with rabbits or eye irritating in rabbits. However, in a clinical assessment inhalation of the vapour of MM by humans was reported to produce a slight irritation of the lungs, skin and eyes.
- In a human patch test hexamethyldisiloxane was not sensitising to the skin.
- In a 28-day repeated oral gavage study with rats the NOAEL was 160 mg/kg bw/day based on reduced food consumption, reduced body weight gain, reduced liver weight, changes to white cell count and corpuscular parameters in male rats.
- In a two-generation reproductive inhalation rat toxicity study the NOAEC for parental toxicity relevant to humans was 400 ppm based on microscopic liver findings in the F0 males of the 5000 ppm group and F1 males and females in the 5000 and 1600 ppm groups.
- In a 28-day repeated dose dermal toxicity study in rats, the no observable effect level (NOEL) for MM was considered to be 500 mg/kg/day, based on reduced kidney and liver weights in males.
- MM did not induce chromosome aberrations in Chines hamster lung cells.
- MM was not mutagenic *in vitro* in the Ames test with *Salmonella typhimurium* bacteria, *Saccharomyces cerevisiae* yeast or in mouse lymphoma L5178Y cells.
- MM did not induce chromosome aberrations in rat bone marrow cells *in vivo*.
- In a long-term (2 years) inhalation study with rats exposed to 100, 400, 1600 and 5000 ppm MM, in the highest exposed, a statistically significant increase in benign Leydig cell tumours in testes of males and enlarged livers in females were observed.
- In a two-generation reproductive toxicity rat study the NOAEC for parental toxicity relevant to humans was 400 ppm based on microscopic liver findings in the F0 males of the 5000 ppm group and F1 males and females in the 5000 and 1600 ppm groups. F0 and F1 reproductive performance was not affected at any concentration. The NOAEC for neonatal toxicity was considered to be 1600 ppm due to decreased F2 offspring weights at 5000 ppm in the F2 generation. The NOAEC for developmental effects was 1600 ppm.

DNELs have been developed for MM:

- For workers via inhalation the DNEL for systemic effects was estimated to 53.4 mg/m^3 based on a NOAEC = 1335 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects showed no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 333 mg/kg bw/day based on a NOAEL = 100 g/kg bw/day and an assessment factor of 300. The NOAEL used was surprisingly high and based on a skin absorption of 0.023% of dose.
- For the general population via inhalation the DNEL for systemic effects was estimated to 13.3 mg/m^3 based on a NOAEC = 664 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated to 167 mg/kg bw/day based on a NOAEL = 100 g/kg bw/day and an assessment factor of 600.
- For the general population via oral route the DNEL for systemic effects was estimated to 0.27 mg/kg bw/day based on a NOAEL = 160 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were foreseen.

Octamethyltrisiloxane (MDM) is registered in REACH (ECHA, 2014i). From the dossier the following information can be extracted:

- The oral (gavage) LD_{50} for acute toxicity (OECD 423) in female rats has been determined at >2 g/kg bw.

- The acute inhalation toxicity (OECD 403) in rats was determined as a $^{4h}LC_{50}$ of 2350 ppm (22.6 mg/L).
- The acute dermal toxicity (OECD 402) in rats was determined as $^{24h}LD_{50}$ > 2 g/kg bw.
- MDM was not skin irritating in rabbits with a 72-h observation period.
- MDM was not sensitising in a guinea-pig maximisation test (OECD Guideline 406).
- In repeated dose 28-day oral (gavage) toxicity with rats (OECD 407) NOAELs were 25 mg/kg/day in the males and 250 mg/kg/day in the females.
- In a sub chronic 90-days inhalation toxicity study (OECD 413) with rats the NOAEL value was 400 ppm. Serious liver and kidney effects were seen at a concentration of 800 ppm in males and 3200 ppm in females.
- MDM was negative in an *in vitro* test of chromosome aberrations in CHO cells (OECD 473).
- MDM was negative with and without metabolic activation in the Ames bacterial mutagenicity test with *Salmonella typhimurium,*
- In a developmental toxicity screening test (OECD422) with rats exposed by inhalation the NOAEC was 3146 ppm.
- MDM did not induce estrogenic or anti-estrogenic effects in the rodent uterotrophic assay following inhalation exposure of rats at 3500 ppm.

DNELs have been developed for MDM:

- For workers via inhalation the DNEL for systemic effects was estimated to 78 mg/m^3 based on a NOAEC = 1945 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 11 mg/kg bw/day based on a NOAEL = 1103 mg/kg bw/day and an assessment factor of 100.
- For the general population via inhalation the DNEL for systemic effects was estimated to 19 mg/m^3 based on a NOAEC = 968 mg/m^3 and an assessment factor of 50.
- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated at 5.6 mg/kg bw/day based on a NOAEL = 1113 mg/kg bw/day and an assessment factor of 200.
- For the general population via oral route the DNEL for systemic effects was estimated to 0.04 mg/kg bw/day based on a NOAEL = 25 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were identified.

Decamethyltetrasiloxane (MD2M) is not classified due to lack of data but it is registered under REACH (ECHA, 2014j). Absorption through intact human skin *in vitro* was insignificant at <0.1%. It is neither skin (OECD404) nor eye irritating. In a seven day oral dose rat study the NOAEL for MD2M was 1000 mg/kg bw/day. In a 28 days oral gavage rat study according to OECD407, the NOAEL was 25 mg/kg bw/day in males and at least 1000 mg/kg bw/day in females. In a rat uterotrophic assay similar to OECD 440, decamethyltetrasiloxane exposure (400 ppm, 6 h/d for 3 days) resulted in a very weak estrogenic response in the luminal epithelial cells only. MD2M was not mutagenic in a mouse lymphoma cell test or in the Ames bacteria test.

DNELs have been developed for MD2M:

- For workers via inhalation the DNEL for systemic effects was estimated at 102 mg/m^3 based on a NOAEC = 2554 mg/m^3 and an assessment factor of 25.
- For workers via inhalation the DNEL for local effects no hazard was identified.
- For workers hazard via dermal route the DNEL for systemic effects was 15 mg/kg bw/day based on a NOAEL = 1449 mg/kg bw/day and an assessment factor of 100.
- For the general population via inhalation the DNEL for systemic effects was estimated at 25 mg/m^3 based on a NOAEC = 5083 mg/m^3 and an assessment factor of 50.

- For the general population via inhalation the DNEL for local effects showed no hazard was identified.
- For the general population via dermal route the DNEL for systemic effects was estimated at 7.3 mg/kg bw/day based on a NOAEL = 1461 mg/kg bw/day and an assessment factor of 200.
- For the general population via oral route the DNEL for systemic effects was estimated at 0.04 mg/kg bw/day based on a NOAEL = 25 mg/kg bw/day and an assessment factor of 600.
- No hazards to skin and eyes were foreseen.

Dodecamethylpentasiloxane (MD3M) is not classified due to lack of data, but it is registered in REACH (ECHA, 2014k). DNELs have been developed on the basis of read across from an inhalation study with MD2M but that is too uncertain. The oral absorption of MD3M in rats is about 25% of administered dose. The elimination was rapid and in 2 days most was excreted, mainly in faeces.

Appendix 2: Environmental assessment for selected siloxanes

Octamethylcyclotetrasiloxane (D4)

The environmental risk assessment reports from the UK Environment Agency concluded that D4 potentially meets the criteria for a PBT substance, when the persistence in sediment is considered, but this conclusion was based on a poorly reported preliminary study (Brooke et al., 2009a). Furthermore, the report mentioned that the half-life for degradation by OH-radicals in the atmosphere was estimated at 12.7-15.8 days. The main degradation process for D4 in water was hydrolysis with a half-life in fresh water (pH 7, 12°C) of 16.7 days, and in sea water (pH 8, 9°C), it was shorter at 2.9 days. The main degradation product formed during the abiotic degradation of D4 was dimethylsilanediol. The properties of D4 mean that it is volatile and also adsorbs strongly onto soil and sediment. A sediment half-life of 123 days at 12°C was determined. Transport to remote areas via air is likely to occur but the substance has a low potential for subsequent deposition to surface media in such regions. Experimental data show that D4 bioconcentrates in fish and is taken up from food. The most reliable value for the steady state BCF was 12,400 in fathead minnow (*Pimephales promelas)* based on total ^{14}C measurements. D4 was not toxic to algae, *Daphnia* and fish at concentrations up to its water solubility limit (0.056 mg/L) (Brooke et al., 2009a).
In November 2008, Environment Canada (2008a) published a screening assessment of D4 with similar conclusions and that D4 had the potential to cause ecological harm.

According to the CLP regulation D4 is classified as aquatic chronic 4 with H413 (ECHA, 2014d). D4 is registered in REACH and has been evaluated as PBT/VPvB (ECHA, 2014e). The vP criterion was fulfilled on the basis of sediment degradation studies. The BCF is above 5,000 in fish. The B and vB criteria were therefore also fulfilled. The T criterion was fulfilled on the basis of both aquatic and mammalian toxicity studies. Thus, D4 met the criteria for a PBT and a vPvB substance in the environment. This conclusion was endorsed by the ECHA PBT Expert Group in November 2012.
In the REACH registration dossier, a hazard assessment was made for aquatic and terrestrial organisms and predators:

- The PNEC for fresh water organisms was 0.44 µg/L with an assessment factor of 10.
- The PNEC for marine water organisms was 0.044 µg/L with an assessment factor of 100.
- The PNEC for STPs was 10 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 0.59 mg/kg sediment dw with an assessment factor of 50.
- The PNEC for marine water sediment was 0.059 mg/kg sediment dw with an assessment factor of 500.
- The PNEC for soil was 0.15 mg/kg soil dw from partition coefficient.
- The PNEC oral for secondary poisoning of predators was 41 mg/kg food with an assessment factor of 90.

Decamethylcyclopentasiloxane (D5)

An environmental risk assessment report from the UK Environment Agency concluded that D5 met the screening criteria for vPvB substances (Brooke et al., 2009b).

The UK Environment Agency assessment also mentioned that D5 had a hydrolysis half-life of 315 days in fresh water at pH 7 and 12°C, but that it was only 43 days in sea water at pH 8 and 12°C. D5 was highly adsorptive to organic matter in sediments and soils. The degradation half-life in sediment was estimated at 800-3100 days. The measured fish BCF was between 2000 and 10.000, but the biomagnification factor (BMF) was small, between 1 and 4. D5 was not toxic to algae, *Daphnia* and fish at concentrations up to its water solubility limit (0.017 mg/L at 23°C) (Brooke et al., 2009b).

In 2009, Environment Canada published a screening study of D5 concluding that D5 could have long-term harmful effects on the environment (EHS Journal, 2011). Later, a Board of Review concluded the opposite: "that Siloxane D5 does not pose a danger to the environment" (Siloxane D5 Board of Review, 2011).

D5 is registered in REACH (ECHA, 2014m). The results of the evaluation of PBT/vPvB properties in REACH was based on the available information, D5 meets the Annex XIII criteria for a vPvB substance in the environment due to its persistence in sediment and high bioconcentration factor in fish. This conclusion was endorsed by the ECHA PBT Expert Group in November 2012 (ECHA, 2014n). D5 is intended to be classified, according to CLP, as Aquatic Chronic 4 (H413) (ECHA, 2014d).

According to a later unpublished 90-days study (OECD 219) on rainbow trout (*Oncorhynchus mykiss*), referred from the REACH dossier, a NOEC of ≥ 14 µg/L was found, and a published 65-days study on fathead minnow (*Pimephales promelas)* found a NOEC ≥ 8.66 µg/L (Parrott et al., 2013). D5 has been shown to cause effects on plants, springtails and earthworms. The lowest reported IC_{50} was 209 mg/kg dry weight in a study with barley (Velicogna et al., 2012).

In the REACH registration dossier, a hazard assessment was made for aquatic andterrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 10 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 11 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 1.1 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazard for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 16 mg/kg food with an assessment factor of 90.

Dodecamethylcyclohexasiloxane (D6)

In 2008, Environment Canada and Health Canada published a screening study of D6 (Environment Canada, 2008b). It was concluded that D6 was persistent in air with calculated atmospheric half-lives of more than 2 days. D6 has the potential to be transported over long distances in the atmosphere. However, it has a low potential to be deposited in water or soil in remote regions. The hydrolysis half-life for D6 is expected to be longer than that of its structurally similar analogues, D4 and D5. D6 was considered persistent under typical Canadian water conditions. In sediment, D6 was expected to have a half-life longer than 49 to 588 days under realistic Canadian sediment conditions, indicating that D6 may be persistent in sediment. D6 was not considered persistent in soil. It was concluded that D6 met the persistence criterion but not the bioaccumulation criterion as set out in the Persistence and Bioaccumulation Regulations.

D6 is classified according to CLP as Aquatic Chronic 4 (H413) (ECHA, 2014d). D6 is registered in REACH (ECHA, 2014g).
In the dossiers the following data was found:

- D6 was not considered a PBT or vPvB substance.
- It was stable in water with a hydrolysis half-life of 42h at pH4, 401 days at pH7 and 125 h at ph9 and 25°C. The degradation product was dimethylsilanediol.
- In a sludge test according to OECD 310, 4.47% of the substance was biodegraded in 28 days.
- A degradation half-life in soil with 32% RH was determined to be 1.38 days.

- A steady-state BCF value of 1160 was determined for fathead minnow (*Pimephales promelas)* and a BCF of 2400 in *Daphnia magna*.
- The partition coefficients air-water and octanol-water were determined as LogKaw = 3.01±0.14 and LogKow = 8.87±0.14.
- In a flow-through fish test (OECD 305), a 49-day NOEC of ≥ 4.4 µg/L was determined for the effects of D6 on mortality of fathead minnow (*Pimephales promelas*).
- In a reproduction test (OECD 211), a 21-day EC_{50} of >4.6 µg/L and a NOEC ≥ 4.6 µg/L were determined for the effects of D6 on reproduction of *Daphnia magna*.
- A 72-hour EC_{50} value of > 2.0 µg/L and a NOEC ≥ 0.1 µg/L have been determined for the effects on growth rate of the alga *Pseudokirchnerella subcapitata*.
- In a respiration inhibition test with activated sludge (OECD 209) the $^{3h}EC_{50}$ was >100 mg/L.
- A 28-day EC_{50} value of 37 mg/kg dw sediment was determined for mortality of the harlequin fly *Chironomus riparius*. A NOEC < 22 mg/kg dw was determined for the effect on development rate and time.
- Data on terrestrial ecotoxicity was either absent or read across.

In the REACH registration dossier for D6, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.8 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 67 mg/kg food with an assessment factor of 300.

Hexamethyldisiloxane (HMDSO)
Hexamethyldisiloxane has been suggested to be classified as Aquatic Acute 1 (H400), Aquatic Chronic 1 (H410) in the notified classification and labelling proposals according to CLP criteria (ECHA, 2014d). MM is registered in REACH (ECHA, 2014h).
In the dossiers the following data was found:

- MM is not considered a PBT or vPvB substance.
- MM is transformed in the air. The dominant gas-phase chemical loss process is by reaction with the OH radical (half-life 11.5 – 17.8 days).
- Hydrolysis half -lives of 1.5, 116 and 12 hours at pH 5, 7 and 9, respectively, were determined at 25°C.
- Biodegradation in water of MM was determined in a test according to OECD Guideline 301 C to 2% in 28 days.
- The rate of degradation in soil increased as the soil became drier, as expected. Degradation half-lives (closed tubes) ranged from 1.8 d at 32% relative humidity and at 22.0°C to 407.6 d at 100% RH and at 22.0°C. The degradation product was mainly trimethylsilanol. The volatilisation was the predominant process for removal of the test substance from soil at 100% RH with a volatilisation half-life of around 3 hours.
- BCF values of 1290 - 2410 L/kg (at 40 µg/L); 776 - 1660 L/kg (at 4 µg/L) have been determined with carp in separate exposures at two concentrations.
- The acute toxicity (mortality) in rainbow trout (*Oncorhynchus mykiss*) was determined as $^{96h}LC_{50}$ of 0.46 mg/L and NOEC of 0.11 mg/L, lower than the water solubility of MM of about 1 mg/L at 23°C.

- In a reproduction test (OECD 211) a 21-day EC_{50} of 0.30 mg/L and a NOEC of 0.08 mg/L were determined as regards the effects of MM on reproduction of *Daphnia magna*.
- A 70-hour EC_{50} value of > 0.55 mg/L and NOEC of 0.1 mg/L have been determined for the effects of MM on growth rate of the microalgae *Pseudokirchnerella subcapitata*.
- In a respiration inhibition test with activated sludge (OECD 209), the $^{3h}EC_{50}$ was >100 mg/L.

In the REACH registration dossier for MM, a hazard assessment was made for aquatic and terrestrial organisms and predators:

- The PNEC for fresh water organisms was 0.002 mg/L with an assessment factor of 10.
- The PNEC for marine water organisms was 0.0002 mg/L with an assessment factor of 100.
- The PNEC for intermittent releases to water was 0.003 mg/L with an assessment factor of 100.
- The PNEC for STPs was 10 mg/L with an assessment factor of 10.
- The PNEC for freshwater sediment was 1.7 mg/kg sediment dw with an assessment factor of 50.
- The PNEC for marine water sediment was 0.17 mg/kg sediment dw with an assessment factor of 500.
- The PNEC for soil was 0.083 mg/kg soil dw from partition coefficient.
- The PNEC oral for secondary poisoning of predators was 67 mg/kg food with an assessment factor of 300.

Octamethyltrisiloxane (MDM)

MDM is not classified or classified as Aquatic Chronic 4 with H413 in the EU notified classification and labelling according to CLP criteria (ECHA, 2014d). MDM is registered in REACH (ECHA, 2014i). In the dossiers the following data was found:

- MDM was not considered a PBT or vPvB substance.
- In a fish acute toxicity test (OECD203), a 96-hour NOEC for mortality of ≥19.4 µg/L was determined for rainbow trout (*Oncorhynchus mykiss*).
- In an early-life stage toxicity test (OECD 210) with rainbow trout the 90-days LOEC was >27 µg/L.
- In a 14-days prolonged toxicity test (OECD204) with juvenile rainbow trout the NOEC was >34 µg/L (saturated solution!).
- In a flow-through fish test (OECD 305) a 42-day NOEC for mortality of ≥34 µg/L (nominal), ≥21 µg/L (mean measured) was determined for fathead minnow (Pimephales promelas).
- In an acute immobilisation test with *Daphnia magna* (OECD 202) the ^{48h}NOEC was > 20 µg/L.
- In a *Daphnia magna* reproduction test (OECD 211) a 21-day EC_{50} (survival and mobility) of >14.3 µg/L was determined, and a NOEC of ≥14.3 µg/L has been determined for effects on growth and reproduction.
- A 72-hour EC_{50} value of >9.4 µg/L and NOEC of ≥9.4 µg/L have been determined for the effects of MDM on growth rate and biomass (yield) of the alga *Pseudokirchnerella subcapitata*.
- A 28-dayEC_{50} of >38 mg/kg dw sediment was determined for the effects on reproduction and biomass of the California blackworm *Lumbriculus variegatus*. A NOEC of 38 mg/kg dw sediment dry weight was determined for the same endpoints.

In the aquatic tests, the concentrations tested were very low and close to the water solubility of MDM of 35 µg/L; therefore, these test results are not very useful.

Environment Canada has developed a Risk Management Scope for MDM in which it was concluded that MDM meets one or more of the criteria as a persistent, bioaccumulative and inherently toxic substance (Environment Canada, 2011). However, in the EU dossier, MDM is not considered a PBT substance.

The important PBT-information about MDM in the dossier was:

- A hydrolysis half-life of 13.7 d (329 h) at pH 7 and 25°C was determined.
- A biodegradation rate of 0% in 28 days was determined.
- The half-lives in soils depend on soil type and relative humidity and ranged from 0.32 days to 120 days.
- In nature, volatilisation was the predominant removal process (half-life <1d).
- In fathead minnows, steady-state BCF values of 5030 l/kg (1.7 µg/l) and 7730 l/kg (21 µg/l) and kinetic BCF values of 3610 l/kg (1.7 µg/l) and 5600 l/kg (21 µg/l) were determined.

In the REACH registration dossier for MDM, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.83 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 0.5 mg/kg soil dw from partition coefficient.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 0.08 mg/kg food with an assessment factor of 300.

Decamethyltetrasiloxane (MD2M)
MD2M is registered in REACH (ECHA, 2014j). The following information is extracted from the dossier:

- MD2M was not considered a PBT or vPvB substance.
- A hydrolysis half-life of 30.3 days (728 h) at pH 7 and 25°C was determined for MD2M. Other tests for degradations were read across from other substances.
- A specific study of bioconcentration with a Flow-through Fish Test (OECD 305) with fathead minnow (*Pimephales promelas).* Steady-state BCF values of 3870 L/kg (0.43 µg/L) and 1610 L/kg (5.3µg/L) and kinetic BCF values of 3830 L/kg (0.43 µg/l) and 1760 L/kg (5.3 µg/L) were determined.
- Adsorption and desorption constants for MD2M were determined as an overall average over three different soils. At 23.7 °C, an adsorption log Koc value of 5.16 and a desorption log Koc value of 5.33 were determined.
- In a fish acute toxicity test (OECD 203) with rainbow trout (*Oncorhynchus mykiss*) a $^{96h}LC_{50}$ and NOEC value of > 6.3 µg/L was determined based on mean measured concentrations.
- In a 35 days study with fathead minnow (*Pimephales promelas)* the NOEC was about the same as above (6.7 µg/L = water solubility).
- In a 21-days *Daphnia magna* Reproduction Test (OECD 211), the NOEC was > 4.9 µg/L.
- In the alga *Pseudokirchnerella subcapitata* growth inhibition test (OECD 201) the ^{72h}NOEC was >2.2 µg/L.
- In all these toxicity tests, the applied concentrations were very low and probably too low to have any chance of causing an adverse effect.
- In a respiration inhibition test with activated sludge (OECD 209), the $^{3h}EC_{50}$ was >100 mg/L.

- No effects on growth and survival were reported when testing MD2M at a loading rate of 100 mg/kg dw sediment (68 mg/kg dwt mean measured) with the freshwater amphipod *Hyallela azteca*. Therefore, a 28-day NOEC value of ≥68 was determined in sediment containing 3.7% organic carbon.
- The tests for terrestrial organisms registered were either data waived, read across or planned studies.

In the REACH registration dossier, a hazard assessment was made for aquatic and terrestrial organisms and predators. There was no potential hazard for air.
Hazards for aquatic organisms were as follows:

- The PNEC for STPs was 1 mg/L with an assessment factor of 100.
- The PNEC for freshwater sediment was 8.3 mg/kg sediment dw with an assessment factor of 10.
- The PNEC for marine water sediment was 0.83 mg/kg sediment dw with an assessment factor of 100.

Hazards for terrestrial organisms were as follows:

- The PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Hazards for predators were as follows:

- The PNEC oral for secondary poisoning of predators was 0.08 mg/kg food with an assessment factor of 300.

Dodecamethylpentasiloxane (MD3M)

Dodecamethylpentasiloxane (MD3M) is not classified due to lack of data, but it is registered in REACH (ECHA, 2014k). Some relevant information is available from the dossier:

- MD3M was not considered a PBT or vPvB substance.
- MD3M has extremely low water solubility. At 23oC it is 70.4±8.3 ng/L.
- In an acute fish toxicity study, according to OECD 203, there was no mortality, and the $^{96h}LC_{50}$ in rainbow trout (*Oncorhynchus mykiss*) was >75 ng/L.
- In a long-term (35-days) test (OECD 305) with MD3M there was no mortality, and the LC_{50} value for fathead minnow (*Pimephales promelas*) was estimated to >39 ng/l.
- In both cases concentrations used in the tests were extremely low (lower than the previous siloxanes); therefore, the relevance of the data for evaluation of MD3M is questionable.

The ecological hazard assessment for aquatic and terrestrial organisms was:

- PNEC for STPs was 1 mg/L with an assessment factor of 100.
- PNEC for freshwater sediment was 1.66 mg/kg sediment dw with an assessment factor of 50.
- PNEC for marine sediment was 0.17 mg/kg sediment dw with an assessment factor of 500.
- PNEC for soil was 3.77 mg/kg soil dw with an assessment factor of 100.

Alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in textiles
The objectives of this study are to identify non-fluorinated alternatives available for surface treatment and impregnation of textiles and to provide environmental and health assessments for the chemical alternatives.

Denne rapport undersøger hvilke tilgængelige ikke-fluorerede alternativer til overfladebehandling og imprægnering af tekstiler der findes, samt deres mulige miljø og sundhedseffekter.

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