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Alternatives to PFASs: Perspectives on the Science

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Poly- and perfluoroalkyl acids (PFASs) are ubiquitous in our lives. These chemicals are used as surfactants and as water and oil repellents in a variety of consumer products such as cosmetics, food packaging, furnishings, and clothing. Since their initial marketing more than 60 years ago, extensive research has demonstrated that the long-chain PFASs are highly persistent, bioaccumulative, and toxic (Buck et al. 2011). As a result, they are being phased out in many countries. However, controversy has emerged regarding the safety of the most common alternatives, the short-chain PFASs.

In the Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs), Blum et al. (2015) question the use of the entire class of PFASs, including short-chain fluorinated alternatives. Authored by 14 experts on the health effects, environmental fate, and policy issues concerning PFASs, the Madrid Statement documents the scientific consensus about the extreme environmental persistence, bioaccumulation, and potential toxicity of the overall class of PFASs (Blum et al. 2015). The statement defines a roadmap for scientists, governments, product manufacturers, purchasing organizations, and consumers to work together to limit the production and use of PFASs globally and to develop safer alternatives. Since it was presented at the 34th International Symposium on Halogenated Persistent Organic Pollutants, held 31 August–5 September 2014 in Madrid, Spain, 206 scientists and professionals from 40 countries have signed the Statement (Blum et al. 2015).

In a response to the Madrid Statement in this issue of *EHP*, the FluoroCouncil, which represents the world's leading fluorotechnology companies, agrees that it "could support many of these policy recommendations if they were limited to long-chain PFASs" (Bowman 2015). The FluoroCouncil supports the call to action from the scientific and professional community to limit the production and environmental release of long-chain PFASs but states that "the short-chain PFAS substances studied to date are not expected to harm human health or the environment," as they "are eliminated more rapidly from the body and are less toxic than long-chain substances" (Bowman 2015).

Although there is agreement regarding the shorter human half-lives of short-chain PFASs, the Helsingør Statement on PFASs (Scheringer et al. 2014) and other recent publications (Gomis et al. 2015; Wang et al. 2013, 2015) expressed concerns that fluorinated replacements are similar to the PFASs they replaced in terms of their chemical structure, environmental persistence, and hazardous potential for both the environment and humans. Given the fact that research raised concern about the long-chain PFASs for many years before action was taken and that global contamination and toxicity have been documented in the general population (Grandjean and Clapp 2014), potential risks of the short-chain PFASs should be taken into account when choosing replacements for the longer-chain compounds.

There are numerous similar examples of replacements for other chemical classes, in which banned or phased-out chemicals have been replaced with structurally similar chemicals. For example, polychlorinated biphenyls were replaced with chlorinated paraffins (National Toxicology Program 2014), polybrominated diphenyl ethers were replaced with other halogenated flame retardants (Birnbaum and Staskal 2004), and bisphenol A has been replaced with bisphenol S, at least in some applications (Rochester and Bolden 2015). Such

straightforward replacement strategies may be cost effective in the short term. However, manufacturers may yet incur costs if the closely related alternative is later found to be as toxic as its predecessor. In fact, there are now multistakeholder efforts to improve the choice of alternatives to chemicals of concern (Birnbaum 2013; National Research Council 2014).

It has been difficult to find substitutes that match the function and performance level of PFASs. The chemical and thermal stability of PFASs as well as their hydrophobic and oleophobic properties provide unique material benefits (Buck et al. 2011). Significant innovation is thus required to find functional nonfluorinated alternatives to PFASs. The U.S. Environmental Protection Agency (EPA) recently recognized such innovation by awarding its 2014 Designing Greener Chemicals Award to a halogen-free firefighting foam (U.S. EPA 2014).

The growing global field of chemical alternatives assessment (CAA) provides tools and strategies for identifying compounds, materials, or product designs to substitute for the use of hazardous chemicals (Lavoie et al. 2010). For example, the California Department of Toxic Substances Control is using CAA in its Safer Consumer Products Program, whose objective is to remove toxic chemicals from products (California Department of Toxic Substances Control 2010). Many CAAs have already been conducted, and many more are in progress (e.g., Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources 2015). Conducting CAAs may prove valuable in clarifying the state of the science among potential alternatives to PFASs and providing guidance for future research and innovation. Nevertheless, finding an optimal alternative substance or technology is not straightforward, and CAAs may not always offer solutions. For instance, suitable nonfluorinated alternatives for certain functions of PFASs, such as stain resistance, appear to be lacking or underdeveloped.

Research is needed to understand the potential for adverse health effects from exposure to the short-chain PFASs, especially regarding low-dose endocrine disruption and immunotoxicity. In parallel, research is needed to find safe alternatives for all current uses of PFASs. The question is, should these chemicals continue to be used in consumer products in the meantime, given their persistence in the environment? And, in the absence of indisputably safe alternatives, are consumers willing to give up certain product functionalities, such as stain resistance, to protect themselves against potential health risks? These conundrums cannot be resolved by science alone but need to be considered in an open discussion informed by the scientific evidence.

In 2012 P.G. prepared an expert report on human health risks from exposure to perfluorinated compounds for the Minnesota Department of Health. L.S.B. declares she has no actual or potential competing financial interests.

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The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

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As scientists and other professionals from a variety of disciplines, we are concerned about the production and release into the environment of an increasing number of poly- and perfluoroalkyl substances (PFASs) for the following reasons:

1. PFASs are man-made and found everywhere. PFASs are highly persistent, as they contain perfluorinated chains that only degrade very slowly, if at all, under environmental conditions. It is documented that some polyfluorinated chemicals break down to form perfluorinated ones (D'Eon and Mabury 2007).
2. PFASs are found in the indoor and outdoor environments, wildlife, and human tissue and bodily fluids all over the globe. They are emitted via industrial processes and military and firefighting operations (Darwin 2011; Fire Fighting Foam Coalition 2014), and they migrate out of consumer products into air (Shoeib et al. 2011), household dust (Björklund et al. 2009), food (Begley et al. 2008; Tittlemier et al. 2007; Trier et al. 2011), soil (Sepulvado et al. 2011; Strynar et al. 2012), ground and surface water, and make their way into drinking water (Eschauzier et al. 2012; Rahman et al. 2014).
3. In animal studies, some long-chain PFASs have been found to cause liver toxicity, disruption of lipid metabolism and the immune and endocrine systems, adverse neurobehavioral effects, neonatal toxicity and death, and tumors in multiple organ systems (Lau et al. 2007; Post et al. 2002). In the growing body of epidemiological evidence, some of these effects are supported by significant or suggestive associations between specific long-chain PFASs and adverse outcomes, including associations with testicular and kidney cancers (Barry et al. 2013; Benbrahim-Tallaa et al. 2014), liver malfunction (Gallo et al. 2012), hypothyroidism (Lopez-Espinosa et al. 2012), high cholesterol (Fitz-Simon et al. 2013; Nelson et al. 2009), ulcerative colitis (Steenland et al. 2013), lower birth weight and size (Fei et al. 2007), obesity (Halldorsson et al. 2012), decreased immune response to vaccines (Grandjean et al. 2012), and reduced hormone levels and delayed puberty (Lopez-Espinosa et al. 2011).
4. Due to their high persistence, global distribution, bioaccumulation potential, and toxicity, some PFASs have been listed under the Stockholm Convention (United Nations Environment Programme 2009) as persistent organic pollutants (POPs).
5. As documented in the Helsingør Statement (Scheringer et al. 2014),
   a. Although some of the long-chain PFASs are being regulated or phased out, the most common replacements are short-chain PFASs with similar structures, or compounds with fluorinated segments joined by ether linkages.
   b. While some shorter-chain fluorinated alternatives seem to be less bioaccumulative, they are still as environmentally persistent as long-chain substances or have persistent degradation products. Thus, a switch to short-chain and other fluorinated alternatives may not reduce the amounts of PFASs in the environment. In addition, because some of the shorter-chain PFASs are less effective, larger quantities may be needed to provide the same performance.
   c. While many fluorinated alternatives are being marketed, little information is publicly available on their chemical structures, properties, uses, and toxicological profiles.
   d. Increasing use of fluorinated alternatives will lead to increasing levels of stable perfluorinated degradation products in the environment, and possibly also in biota and humans. This would increase the risks of adverse effects on human health and the environment.
6. Initial efforts to estimate overall emissions of PFASs into the environment have been limited due to uncertainties related to product formulations, quantities of production, production locations, efficiency of emission controls, and long-term trends in production history (Wang et al. 2014).
7. The technical capacity to destroy PFASs is currently insufficient in many parts of the world.

Global action through the Montreal Protocol (United Nations Environment Programme 2012) successfully reduced the use of the highly persistent ozone-depleting chlorofluorocarbons (CFCs), thus allowing for the recovery of the ozone layer. However, many of the organofluorine replacements for CFCs are still of concern due to their high global warming potential. It is essential to learn from such past efforts and take measures at the international level to reduce the use of PFASs in products and prevent their replacement with fluorinated alternatives in order to avoid long-term harm to human health and the environment.

For these reasons, we call on the international community to cooperate in limiting the production and use of PFASs and in developing safer nonfluorinated alternatives. We therefore urge scientists, governments, chemical and product manufacturers, purchasing organizations, retailers, and consumers to take the following actions:

Scientists:

1. Assemble, in collaboration with industry and governments, a global inventory of all PFASs in use or in the environment, including precursors and degradation products, and their functionality, properties, and toxicology.
2. Develop analytical methods for the identification and quantification of additional families of PFASs, including fluorinated alternatives.
3. Continue monitoring for legacy PFASs in different matrices and for environmental reservoirs of PFASs.
4. Continue investigating the mechanisms of toxicity and exposure (e.g., sources, fate, transport, and bioaccumulation of PFASs), and improve methods for testing the safety of alternatives.
5. Bring research results to the attention of policy makers, industry, the media, and the public.

Governments:

1. Enact legislation to require only essential uses of PFASs, and enforce labeling to indicate uses.
2. Require manufacturers of PFASs to
   a. conduct more extensive toxicological testing,
   b. make chemical structures public,
   c. provide validated analytical methods for detection of PFASs, and
   d. assume extended producer responsibility and implement safe disposal of products and stockpiles containing PFASs.
3. Work with industry to develop public registries of products containing PFASs.
4. Make public annual statistical data on production, imports, and exports of PFASs.

5. Whenever possible, avoid products containing, or manufactured using, PFASs in government procurement.
6. In collaboration with industry, ensure that an infrastructure is in place to safely transport, dispose of, and destroy PFASs and PFAS-containing products, and enforce these measures.

Chemical manufacturers:

1. Make data on PFASs publicly available, including chemical structures, properties, and toxicology.
2. Provide scientists with standard samples of PFASs, including precursors and degradation products, to enable environmental monitoring of PFASs.
3. Work with scientists and governments to develop safe disposal methods for PFASs.
4. Provide the supply chain with documentation on PFAS content and safe disposal guidelines.
5. Develop nonfluorinated alternatives that are neither persistent nor toxic.

Product manufacturers:

1. Stop using PFASs where they are not essential or when safer alternatives exist.
2. Develop inexpensive and sensitive PFAS quantification methods for compliance testing.
3. Label products containing PFASs, including chemical identity and safe disposal guidelines.
4. Invest in the development and use of nonfluorinated alternatives.

Purchasing organizations, retailers, and individual consumers:

1. Whenever possible, avoid products containing, or manufactured using, PFASs. These include many products that are stain-resistant, waterproof, or nonstick.
2. Question the use of such fluorinated "performance" chemicals added to consumer products.

The views expressed in this statement are solely those of the authors and signatories. The authors declare they have no actual or potential competing financial interests.

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Fluorotechnology Is Critical to Modern Life: The FluoroCouncil Counterpoint to the Madrid Statement

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The Madrid Statement (Blum et al. 2015) is a listing of policy recommendations that its authors would apply to a broad universe of poly- and perfluoroalkyl substances (PFASs). The FluoroCouncil could support many of these policy recommendations if they were limited to long-chain PFASs. However, the application of these recommendations to a broad universe of PFASs simply cannot be supported.

The core weakness of the document is the absence of a compelling rationale for the sweeping scope of those recommendations. Specifically, the Madrid Statement fails as a policy statement in the following areas:

1. It does not acknowledge the fact that fluorotechnology is essential technology for many aspects of modern life, a critical consideration for adoption of any social policy on PFASs.
2. It ignores a large body of scientific information demonstrating important differences between the health and environmental impacts of long-chain and short-chain PFASs. The U.S. Environmental Protection Agency (EPA) and other regulators have approved numerous short-chain alternatives to replace long-chain PFASs. Data in non-human primates indicate shorter-chain perfluoroalkyl carboxylic acids (PFCAs) are less toxic than long-chain PFCAs and have substantially shorter half-lives than perfluorooctanoic acid (PFOA) in particular (U.S. EPA 2015a).
3. It does not recognize the substantial and continuing efforts by industry and governments to replace long-chain substances with alternatives that limit environmental impacts while continuing to provide the unique benefits of PFAS chemistry. These efforts continue, but more work is needed by all parties to complete this transition.

In our daily life we rely on fluorotechnology, mostly without noticing, because it uniquely enhances the functionality and durability of things we take for granted, such as airplanes, automobiles, and cell phones. PFASs are designed for specific end uses, and therefore all PFAS chemistry is not the same. In fact, the term "PFAS" describes a large class of chemistries. Although FluoroCouncil member companies do not participate in all these chemistries, we have expertise in two types of chemistries that are important to everyday life: fluoropolymers and fluorotelomers.

Fluoropolymers have unmatched thermal and chemical stability, providing strength, resilience, and durability for the reliable function of a variety of products and industries. Chemical and pharmaceutical manufacturers rely on this technology in linings for pipes, valves, and tanks to allow safe and clean production of products we use and consume every day. Aircraft, trucks, buses, and cars utilize high-reliability, durable, lightweight tubing and hoses made from fluoropolymers that reduce overall weight and prevent evaporation of fuel vapors, reducing greenhouse gas emissions and increasing fuel efficiency. In addition, fluoropolymers exhibit unique dielectric properties that enable high-speed data transfer for wireless communications in smart phones and other devices.

Fluorotelomer-based polymers provide protective surface finishes for textiles such as surgical gowns and drapes that shield against fluid-borne pathogens, protecting patients and health care workers. These products are also used on uniforms to protect chemical workers, military personnel, and firefighters, as well as on outerwear and gear for outdoor enthusiasts, so that all can return home safely. The unique property of water and oil repellency is also utilized in specialized paper and paperboard applications to prevent burns from hot oil in food preparation and to protect food from spoilage. One key use for fluorotelomer-based surfactants is in firefighting foams. These foams extinguish aircraft and oilfield fires faster and provide more protection from reignition than any other medium, saving lives of first responders, military personnel, and others while also protecting property. More information on the uses and benefits of fluorotechnology is available on the FluoroCouncil website (http://www.fluorocouncil.org).

Given this range of important societal benefits offered by fluorotechnology, policy measures on PFASs need to be strongly supported by rigorous risk assessment based on all relevant data.

In response to public concerns that arose over PFOA and perfluorooctanesulfonic acid (PFOS) more than a decade ago, the FluoroCouncil member companies developed new products, including PFASs based on short chains, which provide comparable properties and benefits to long-chain products, often at similar concentrations, with improved health and environmental profiles.

For the past several years, FluoroCouncil member companies have engaged in an ambitious program to develop robust scientific data on these alternative products, the raw materials used to produce them, and their degradation products. Although a broad scientific discussion continues regarding how much science is needed to assess these short-chain products, significant toxicity and environmental data have been provided to regulators globally for systematic chemical review processes. Some of these data have been published in the scientific literature.

We would welcome the opportunity to collaborate with the broader community to establish a publicly accessible website housing the available scientific literature references on short-chain PFASs. Our efforts in international fora to create a public reference database for this literature have not yet been successful. However, these products have undergone rigorous review in the registration processes of multiple government agencies and are approved for use. Any claim that there are minimal data publicly available on the hazards and risks of these substances is simply incorrect.

This robust set of published data as well as data submitted to regulatory authorities support the conclusion that the short-chain PFASs studied to date are not expected to harm human health or the environment. Although the structures of short-chain PFASs may be similar to their long-chain equivalents, data show the short-chain chemistry in general is very different from the long-chain chemistry. For example, short-chain substances are eliminated more rapidly from the body and are less toxic than long-chain substances (Borg et al. 2013; ENVIRON International Corp. 2014; Gannon et al. 2011; Han et al. 2012; Iwai and Hoberman 2014; Martin et al. 2003a, 2003b; Russell et al. 2013).

Any assessment of the alternatives to long-chain PFASs must be based on all the relevant factors that have historically guided risk assessment, including the cornerstone considerations of a substance's hazard and exposure potential. Some critiques of PFASs have relied solely on the fact that these substances are persistent in the environment, a feature that is often closely related to their technological strengths as durable materials. Decisions on the societal acceptability of strategic materials such as PFASs cannot be wisely made on a single attribute such as persistence.

If the Madrid Statement had been directed at long-chain PFASs rather than the larger universe of substances it addresses, the FluoroCouncil would have been supportive of many of the policy measures described. Nearly a decade ago, in response to questions about the presence of long-chain PFCAs and their precursors in the environment and in living systems, FluoroCouncil members were among the industry leaders that took action. In 2006 the FluoroCouncil member companies voluntarily committed to a global phaseout of long-chain products and related plant emissions by the end of 2015. This program, known as the U.S. EPA 2010/2015 PFOA Stewardship Program, has resulted in dramatic reductions in environmental emissions from manufacturing and products, concurrent with development and introduction of short-chain alternatives (U.S. EPA 2015b). A similar program was successfully implemented in cooperation with Environment Canada and Health Canada (Environment Canada 2013). Demonstrable success of these programs has been shown in the reduction of measurable levels of long-chain PFCAs in the environment and in living systems (Centers for Disease Control and Prevention 2014; Health Canada 2013). This was achieved well ahead of regulation.

The global elimination of long-chain PFASs should be a common goal shared by the FluoroCouncil members, governments, and a wide range of other stakeholders. The FluoroCouncil has strongly advocated for science-based regulation of long-chain PFASs. To truly address these priority chemicals, it is critical that regulatory authorities and other stakeholders focus on eliminating the production and use of products and articles made from or containing long-chain PFASs. Completing that transition should be the centerpiece of policy on PFASs.

The members of the FluoroCouncil have engaged in stewardship activities for several years and recognize the value of continually enhancing their chemistries and products while being mindful of the environment, health, and safety. We remain ready to engage with governments and other stakeholders in refining our approach. We believe there may be opportunities for constructive dialogue in the following areas:

1. Strategies to complete the transition away from long-chain PFASs, a clear area of common ground.
2. Identification of areas that warrant further information development and risk assessment.
3. Actions that can foster additional stewardship activities within the supply chain, such as the guidance document on best environmental practices in textile manufacturing recently issued by the FluoroCouncil (FluoroCouncil 2014).
4. Best methods for sharing with all stakeholders, including the scientific community, information on PFASs that is relevant to the health and environmental impact of fluorotechnology.

In pursuing these or any other topics of mutual interest, it will be important that all stakeholders recognize that policy on PFASs must necessarily consider the importance of fluorotechnology in many areas of society. Any policy discussion should be based on well-established risk assessment principles that weigh the hazard and exposure potential of specific substances and should include the implementation of best practices to reduce the potential for exposure while preserving the essential societal benefits of fluorotechnology.

The author is employed by the American Chemistry Council and manages the FluoroCouncil, a global organization representing the world's leading fluorotechnology companies, with a primary focus on fluoropolymers and fluorotelomer-based performance products. The members of the FluoroCouncil are Archroma Management LLC, Arkema France, Asahi Glass Co., Ltd., Daikin Industries, Ltd., DuPont Company, and Solvay Specialty Polymers.

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