



Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs)



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ABSTRACT

In this discussion paper, the transition from long-chain poly- and perfluorinated alkyl substances (PFASs) to fluorinated alternatives is addressed. Long-chain PFASs include perfluoroalkyl carboxylic acids (PFCAs) with 7 or more perfluorinated carbons, perfluoroalkyl sulfonic acids (PFASs) with 6 or more perfluorinated carbons, and their precursors. Because long-chain PFASs have been found to be persistent, bioaccumulative and toxic, they are being replaced by a wide range of fluorinated alternatives. We summarize key concerns about the potential impacts of fluorinated alternatives on human health and the environment in order to provide concise information for different stakeholders and the public. These concerns include, amongst others, the likelihood of fluorinated alternatives or their transformation products becoming ubiquitously present in the global environment; the need for more information on uses, properties and effects of fluorinated alternatives; the formation of persistent terminal transformation products including PFCAs and PFASs; increasing environmental and human exposure and potential of adverse effects as a consequence of the high ultimate persistence and increasing usage of fluorinated alternatives; the high societal costs that would be caused if the uses, environmental fate, and adverse effects of fluorinated alternatives had to be investigated by publicly funded research; and the lack of consideration of non-persistent alternatives to long-chain PFASs.

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Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs)

We as scientists working on the characterization of the uses, properties, analysis, environmental distribution and adverse effects of poly- and perfluorinated alkyl substances, PFASs, are concerned that long-chain PFASs are being replaced by a wide range of fluorinated alternatives for which we have only little information on production volumes, uses, properties and biological effects. Nevertheless, we do know that these replacements will be similarly resistant to ultimate degradation, i.e. persistent, in the environment as long-chain PFASs (Scheringer et al., 2013; Strempel et al., 2012).

By long-chain PFASs we denote perfluoroalkyl carboxylic acids (PFCAs) with 7 or more perfluorinated carbons, perfluoroalkyl sulfonic acids (PFASs) with 6 or more perfluorinated carbons, and their precursors such as fluorotelomer-based substances with 8 or more perfluorinated carbons and perfluoroalkane sulfonyl fluoride-based substances with 6 or more perfluorinated carbons. The terminology for nomenclature of PFASs used herein has been proposed by Buck et al. (2011).

In the absence of clear evidence that the alternatives are a substantial improvement on long-chain PFASs, we think that it is not sufficient that the substitution process of long-chain PFASs leads to just an incremental shift in the type of products that are placed on the global market and will be used by millions of consumers and professional users. In this situation, we would like to bring the following statement to the attention of policy makers and various relevant stakeholders.

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1. PFASs are ubiquitous.

A wide range of PFASs, including fluorinated alternatives to long-chain PFASs, is present in environmental matrices (Giesy and Kannan, 2002; McLachlan et al., 2007; Ahrens, 2011; Li et al., 2011; Eschauzier et al., 2012; Müller et al., 2012; Zhao et al., 2012; Gawor et al., 2013; Wang et al., 2013; Zareitalabad et al., 2013), wildlife (Giesy and Kannan, 2002; Houde et al., 2011), and human tissue (Giesy and Kannan, 2002; Kannan et al., 2004; Martin et al., 2010; Kato et al., 2011; Loi et al., 2013; Yeung et al., 2013a,b) all over the globe.

2. Regulation has caused levels of some PFAS to decline, but others remain stable or continue to increase.

Because perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and PFCAs with 11–14 perfluorinated carbons have been shown to be highly persistent and also bioaccumulative and toxic, these substances are now regulated in the EU and Canada and there have been several voluntary actions by the manufacturing industry to phase out or reduce the emissions of these substances (EU, 2006; Canada Gazette, 2013; ECHA, 2014; US EPA, 2006); PFOS is also regulated globally under the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2014). These regulations were established already after a decade of intense scientific research. As a consequence of phase-out actions and regulations, levels of PFOS and PFOA in human blood samples have now declined in many Western countries (Glynn et al., 2012; Kato et al., 2011; Harada et al., 2010; Yeung et al., 2013a). However, PFCAs with longer perfluorinated chains than PFOA, with 8 or more perfluoroalkyl carbons, have not yet shown signs of decline in human blood samples globally (Kato et al., 2011; Glynn et al., 2012; Yeung et al., 2013b).

3. More information on fluorinated alternatives is urgently needed.

Currently, a wide range of fluorinated alternatives to long-chain PFASs are being developed and commercialized (OECD, 2013; Wang et al., 2013). Many of these fluorinated alternatives are shorter-chain homologues of long-chain PFASs (typically with 6 or fewer perfluoroalkyl carbons). This has the advantage of making the substances less bioaccumulative than long-chain PFASs, but the perfluorinated chain is still recalcitrant to degradation. Moreover, shorter-chain alternatives are not always less bioaccumulative; there is evidence of higher uptake into maize shoots compared to long-chain PFASs (Krippner et al., 2014). In many cases there is only very limited knowledge in the public domain on the structures, properties, uses and toxicological profiles of fluorinated alternatives. The levels of some fluorinated alternatives or their degradation products, such as perfluorobutane sulfonic acid (PFBS) or perfluorobutanoic acid (PFBA), have been shown to be rising in recent years in the environment and human tissues in Europe (Glynn et al., 2012; Ahrens, 2011; Kirchgeorg et al., 2013). There is an urgent need to provide the necessary knowledge on the environmental and human health risks of this rapidly expanding range of fluorinated compounds, in a way that makes the information publicly accessible.

4. Less efficient fluorinated alternatives may lead to increased use, emissions, and exposure.

While the shorter-chain PFASs are being introduced because they are generally less bioaccumulative, in some cases their technical performance is lower (Renner, 2006; Daikin, 2009; Archroma,

2013) and so there is a concern that larger quantities and/or more substances will need to be used to provide the same performance, potentially cancelling out the benefit of lower bioaccumulation potential.

5. Concerns about low testing requirements.

In the EU the testing requirements under REACH are defined by the production volume of a chemical. In cases where mixtures or combinations of fluorinated alternatives are used to replace a single long-chain PFAS, the amounts of the individual substances may be smaller than the amount of the long-chain PFAS to be replaced so that also the testing requirements are lower. Furthermore, we are concerned that current testing requirements are not sufficient to identify effects such as immunotoxicity and endocrine disruption, which have been linked to PFAS exposure (Grandjean and Budtz-Jørgensen, 2013; White et al., 2011).

6. Regulations need to be established in an increasing number of countries producing and applying PFASs.

PFASs including fluorinated alternatives are manufactured by an increasing number of producers and in more and more regions of the world. As a consequence, the regulation of PFASs needs to be implemented in more countries than in the past. The types of products available on the global market are also more diverse and difficult to characterize.

7. PFASs, including fluorinated alternatives, lead to highly persistent transformation products, which implies increasing human and environmental exposure.

In spite of the diversity of the fluorinated alternatives, current knowledge demonstrates that the perfluorinated parts of fluorinated alternatives are recalcitrant and will form terminal transformation products, including PFCAs and PFSAs (Lee et al., 2010; Young and Mabury, 2010; Liu and Mejia Avendaño, 2013; Butt et al., 2014), which are persistent in the environment (Hurley et al., 2004; Liou et al., 2010; Vaalgamaa et al., 2011; Liu et al., 2013). Extensive and increasing use and emissions of fluorinated alternatives will lead to increasing levels of PFCAs, PFSAs and other stable perfluorinated degradation products in the environment, biota and humans.

8. Increasing exposure implies increasing risk of adverse effects.

It is therefore likely that the fluorinated alternatives or their transformation products will lead to large-scale environmental and human exposure to a range of PFASs and possibly result in adverse effects caused by these substances. As a consequence, we are concerned that the current introduction of fluorinated alternatives eventually may lead to similar problems as occurred in the cases of PFOS and long-chain PFCAs. If the highly persistent and environmentally mobile fluorinated alternatives are shown to cause adverse effects in the future, it may take decades to reverse global contamination to safe levels.

9. It is costly for society to produce new toxicological data; therefore data produced by chemical manufacturers should be made publicly available.

It would be an expensive and time-consuming process to initiate years of publicly funded research into the properties and potential effects of the fluorinated alternatives. Therefore, all data

on the chemical and toxicological properties of fluorinated alternatives collected by manufacturers and suppliers that are not currently publicly available should be made accessible. In addition to the cost to society of publicly funded risk assessment, there is the risk that there will be an irreversible global environmental problem caused by the widespread occurrence of these fluorinated alternatives and/or their transformation products.

10. Non-persistent alternatives to long-chain PFASs should be used to protect clean food and water resources for a growing human population.

The goal should be to introduce non-persistent alternatives that can be fully degraded and mineralized, and this may imply non-fluorinated products. Therefore, development of non-persistent alternatives should be strongly encouraged and PFASs should only be used in applications where they are truly needed and proven indispensable.

References

- Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* 13, 20–31.
- Archroma, 2013. Regulatory affairs. The challenge PFOA free. <<https://www.performancedays.eu/regulatory-affairs-the-challenge-pfoa-free.html>>.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., et al., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr. Environ. Assess. Manage.* 7, 513–541.
- Butt, C.M., Muir, D.C.G., Mabury, S.A., 2014. Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: a review. *Environ. Toxicol. Chem.* 33, 243–267.
- Canada Gazette, 2013. Order Adding Toxic Substances to Schedule 1 to the Canadian Environmental Protection Act, 1999. <<http://www.gazette.gc.ca/rp-pr/p2/2013/2013-11-06/html/sor-dors188-eng.php>>.
- Daikin, 2009. Effort to reduce the environmental emissions of PFOA and to develop the alternative products (Daikin Example). <http://www.chem.unep.ch/unepsaicm/cheminprod_dec08/PFCWorkshop/Presentations/Daikin.pdf>.
- EU, 2006. Directive 2006/122/EC of the European Parliament and of the Council. Official Journal of the European Union, 27 December 2006.
- ECHA, 2014. Candidate list of substances of very high concern for authorisation. European Chemicals Agency, Helsinki. <<http://echa.europa.eu/candidate-list-table>>.
- Eschauer, C., de Voogt, P., Brauch, H.J., Lange, F.T., 2012. Perfluorinated Chemicals in European Surface Waters, Ground- and Drinking Waters. In: Knepper, T.P., Lange, F.T. (Eds.), *Polyfluorinated chemicals and transformation products. Handbook of Environmental Chemistry*, vol. 17, pp. 73–102.
- Gawor, A., Shunthirasingham, C., Hayward, S.J., Lei, Y.D., Gouin, T., Mmereki, B.T., et al., 2013. Neutral polyfluoroalkyl substances in the global atmosphere. *Environ. Sci. Process. Impacts* 16, 404–413.
- Giesy, J.P., Kannan, K., 2002. Perfluorochemical surfactants in the environment. *Environ. Sci. Technol.* 36, 146A–152A.
- Glynn, A., Berger, U., Bignert, A., Ullah, S., Aune, M., Lignell, S., Darnerud, P.O., 2012. Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: serial sampling during pregnancy and nursing, and temporal trends 1996–2010. *Environ. Sci. Technol.* 46, 9071–9079.
- Grandjean, P., Budtz-Jørgensen, E., 2013. Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children. *Environ. Health* 12, 35.
- Harada, K.H., Yang, H.R., Moon, C.S., Hung, N.N., Hitomi, T., Inoue, K., et al., 2010. Levels of perfluorooctane sulfonate and perfluorooctanoic acid in female serum samples from Japan in 2008, Korea in 1994–2008 and Vietnam in 2007–2008. *Chemosphere* 79, 314–319.
- Houde, M., De Silva, A.O., Muir, D.C.G., Letcher, R.J., 2011. Monitoring of perfluorinated compounds in aquatic biota: an updated review. *Environ. Sci. Technol.* 45, 7962–7973.
- Hurley, M., Andersen, M., Wallington, T., Ellis, D., Martin, J., Mabury, S., 2004. Atmospheric chemistry of perfluorinated carboxylic acids: reaction with OH radicals and atmospheric lifetimes. *J. Phys. Chem. A* 108, 615–620.
- Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K.S., Loganathan, B.G., et al., 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ. Sci. Technol.* 38, 4489–4495.
- Kato, K., Wong, L.-Y., Jia, L.T., Kuklenyik, Z., Calafat, A.M., 2011. Trends in exposure to polyfluoroalkyl chemicals in the U.S. population: 1999–2008. *Environ. Sci. Technol.* 45, 8037–8045.
- Kirchgeorg, T., Dreyer, A., Gabrieli, J., Kehrwald, N., Sigl, M., Schwikowski, M., et al., 2013. Temporal variations of perfluoroalkyl substances and polybrominated diphenyl ethers in alpine snow. *Environ. Pollut.* 178, 367–374.
- Krippner, J., Brunh, H., Falk, S., Georgii, S., Schubert, S., Stahl, T., 2014. Effects of chain length and pH on the uptake and distribution of perfluoroalkyl substances in maize (*Zea mays*). *Chemosphere* 94, 85–90.
- Lee, H., D'Eon, J., Mabury, S.A., 2010. Biodegradation of Polyfluoroalkyl Phosphates as a Source of Perfluorinated Acids to the Environment. *Environ. Sci. Technol.* 44, 3305–3310.
- Li, J., Del Vento, S., Schuster, J., Zhang, G., Chakraborty, P., Kobara, Y., Jones, K.C., 2011. Perfluorinated compounds in the Asian atmosphere. *Environ. Sci. Technol.* 45, 7241–7248.
- Liou, J.S.C., Szostek, B., DeRito, C.M., Madsen, E.J., 2010. Investigating the biodegradability of perfluorooctanoic acid. *Chemosphere* 80, 176–183.
- Liu, D., Xiu, Z., Liu, F., Wu, G., Adamson, D., Newell, C., et al., 2013. Perfluorooctanoic acid degradation in the presence of Fe(III) under natural sunlight. *J. Hazard. Mater.* 262, 456–463.
- Liu, J., Mejia Avendaño, S., 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: a review. *Environ. Int.* 61, 98–114.
- Loi, E.I.H., Yeung, L.W.Y., Mabury, S.A., Lam, P.K.S., 2013. Detections of commercial fluorosurfactants in Hong Kong marine environment and human blood: a pilot study. *Environ. Sci. Technol.* 47, 4677–4685.
- Martin, J.W., Asher, B.J., Beeson, S., Benskin, J.P., Ross, M.S., 2010. PFOS or PreFOS? are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* 12, 1979–2004.
- McLachlan, M.S., Holmström, K.E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European continent. *Environ. Sci. Technol.* 41, 7260–7265.
- Müller, C.E., Gerecke, A.C., Bogdal, C., Wang, Z., Scheringer, M., Hungerbühler, K., 2012. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day-night patterns of air concentrations in summer in Zurich, Switzerland. *Environ. Pollut.* 169, 196–203.
- OECD, 2013. OECD/UNEP Global PFC Group, Synthesis Paper on Per- and Polyfluorinated Chemicals (PFCs). Environment, Health and Safety, Environment Directorate, OECD, Paris, France. <http://www.oecd.org/env/ehs/risk-management/PFC_FINAL-Web.pdf>.
- Renner, R., 2006. The long and the short of perfluorinated replacements. *Environ. Sci. Technol.* 40, 12–13.
- Scheringer, M., Stempel, S., Ng, C.A., Hungerbühler, K., 2013. Response to comment on screening for PBT chemicals among the “Existing” and “New” chemicals of the EU. *Environ. Sci. Technol.* 47, 6065–6066.
- Stempel, S., Scheringer, M., Ng, C.A., Hungerbühler, K., 2012. Screening for PBT chemicals among the “Existing” and “New” chemicals of the EU. *Environ. Sci. Technol.* 46, 5680–5687.
- UNEP, 2014. Stockholm Convention on Persistent Organic Pollutants. <<http://www.pops.int>>.
- US EPA, 2006. 2010/15 PFOA Stewardship Program; United States Environmental Protection Agency (US EPA). <<http://www.epa.gov/oppt/pfoa/pubs/stewardship>>.
- Vaalgamaa, S., Vähätalo, A.V., Perkola, N., Huhtala, S., 2011. Photochemical reactivity of perfluorooctanoic acid (PFOA) in conditions representing surface water. *Sci. Total Environ.* 409, 3043–3048.
- Wang, Z., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCA), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environ. Int.* 60, 242–248.
- White, S.S., Fenton, S.E., Hines, E.P., 2011. Endocrine disrupting properties of perfluorooctanoic acid. *J. Steroid Biochem. Mol. Biol.* 127, 16–26.
- Yeung, L.W.-Y., Robinson, S., Koschorreck, J., Mabury, S.A., 2013a. Part II. A temporal study of PFOS and its precursors in human plasma from two German cities in 1982–2009. *Environ. Sci. Technol.* 47, 3875–3882.
- Yeung, L.W.-Y., Robinson, S., Koschorreck, J., Mabury, S.A., 2013b. Part I. A temporal study of PFCA and its precursors in human plasma from two German cities 1982–2009. *Environ. Sci. Technol.* 47, 3865–3874.
- Young, C.J., Mabury, S.A., 2010. Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. *Rev. Environ. Contam. Toxicol.* 208, 1–109.
- Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W., 2013. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – a review on concentrations and distribution coefficients. *Chemosphere* 91, 725–732.
- Zhao, Z., Xie, Z., Möller, A., Sturm, R., Tang, J., Zhang, G., Ebinghaus, R., 2012. Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast. *Environ. Pollut.* 170, 71–77.