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Technical work: guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals

Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals

Note by the Secretariat

The annex to the present note sets out the guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals, as endorsed by the Persistent Organic Pollutants Review Committee at its ninth meeting. The annex has not been formally edited.

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Annex

Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals

18 October 2013

Disclaimer

The present document is a status report based on available information on alternatives to perfluorooctane sulfonic acid (PFOS) and its related chemicals. It is important to note that toxicological and ecotoxicological data gaps remain with regard to potential alternatives to PFOS and its related chemicals. The data presented in the document are only suggestive, and it is important that research continue with the aim of yielding additional health and environmental data that will enable a better understanding of the toxicological and ecotoxicological effects of the alternatives presented. The document responds to specific issues relating to the Stockholm Convention and does not address issues unrelated to persistent organic pollutants.

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List of abbreviations and acronyms

AFFF	aqueous film-forming foams
AR-AFFF	alcohol-resistant aqueous film-forming foams
AR-FFFP	alcohol-resistant film-forming fluoroprotein foams
BCF	bioconcentration factor
CAS	Chemical Abstract Service
CCD	charge-coupled device (technology for capturing digital images)
CEN	European Committee for Standardization
D4	octamethyl cyclotetrasiloxane
D5	decamethyl cyclopentasiloxane
D6	dodecamethyl cyclohexasiloxane
diPAPs	diesters of polyfluoroalkyl phosphonic acids and phosphoric acids
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ETFE	ethylene tetrafluoroethylene
EtFOSA	*N*-ethyl perfluorooctane sulfonamide (sulfluramid)
EtFOSE	*N*-ethyl perfluorooctane sulfonamidoethanol
EtFOSEA	*N*-ethyl perfluorooctane sulfonamidoethyl acrylate
EtFOSEP	di[*N*-ethyl perfluorooctane sulfonamidoethyl] phosphate
EU	European Union
F-53	potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate/perfluoro[hexyl ethyl ether sulfonate]
F-53B	potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
FC-80	PFOS potassium salt
FC-98	potassium perfluoroethyl cyclohexyl sulfonate
FC-248	PFOS tetraethyl ammonium salt
FFFP	film-forming fluoroprotein foams
INCI	International Nomenclature of Cosmetic Ingredients
LD_{50}	doses that killed 50%
MeFOSA	*N*-methyl perfluorooctane sulfonamide
MeFOSE	*N*-methyl perfluorooctane sulfonamidoethanol
MeFOSEA	*N*-methyl perfluorooctane sulfonamidoethyl acrylate OECD
MDM	octamethyl trisiloxane
MD2M	decamethyl tetrasiloxane
MD3M	dodecamethyl pentasiloxane
MM (or HMDSO)	hexamethyl disiloxane
NGLF	Norsk Galvanoteknisk Landsforening
NOAEC	No observable adverse effect concentration
NOAEL	No observable adverse effect level
OECD	the Organisation for Economic Co-operation and Development
PAPs	polyfluoroalkyl phosphonic acids and phosphoric acids
PFAAs	perfluoroalkanoic acids
PFAS	perfluorinated alkyl sulfonates
PFBS	perfluorobutane sulfonic acid/potassium perfluorobutane sulfonate
PFBSF	perfluorobutane sulfonyl fluoride
PFBSK	PFBS potassium salt
PFCs	polyfluorinated chemicals
PFCA	perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoic acid

PFDS	perfluorodecane sulfonic acid
PFHpA	perfluoroheptanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFOSA	perfluorooctane sulfonamide
PFOSF	perfluorooctane sulfonyl fluoride
PTFE	polytetrafluoroethylene
ZVO	German national metal plating association
QSAR	quantitative-structure-activity-relationships

Executive summary

1. At its fourth meeting the Conference of the Parties to the Stockholm Convention decided that the production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) should be eliminated by all parties except for the use and production allowed as acceptable purposes and specific exemptions in accordance with Part III of Annex B to the Convention. While the PFOS related chemicals used in practice may not themselves be specifically listed in the Convention, their production and use is restricted by the listing of PFOS, its salts and PFOSF.

2. The objective of the present study is to summarize what is currently known about alternatives to PFOS, its salts, PFOSF and their related chemicals, and to enhance the capacity of developing countries and countries with economies in transition to phase out PFOS, its salts and PFOSF taking into account the need for longer phase-in schedules for alternatives for some uses and the fact that for certain uses alternatives may not be currently readily available in all countries.

3. The present paper discusses the various uses of PFOS, its salts and PFOSF as a surfactant in impregnation, coating, metal plating, fire-fighting foams and the like and indicates where alternatives have been suggested, are available or have already been introduced to the market. Fluorinated or non-fluorinated alternatives exist for nearly all current uses. Available alternatives may not be ideal and are not necessarily economically and technically equivalent to PFOS; they may also pose environmental and health hazards at a certain level.

4. Fluorosurfactants are extremely persistent and provide low surface tension. PFOS performs well in this regard. However due to environmental and health concerns, other surfactants with or without fluorine could be used as alternatives depending on the application and function required. Given the relatively high prices of some fluorosurfactants, switching to alternatives can in some cases also have economic benefits.

5. The most common PFOS alternatives in use are fluorotelomers, which are precursors for perfluoroalkyl carboxylic acids (PFCA). Formerly the choice was often C_8-fluorotelomers; those substances, however, have been shown to degrade into perfluorooctanoic acid (PFOA), whose hazardous and long-range transport properties are also cause for concern. For that reason some producers of fluorochemicals in the EU, Japan, and US have voluntarily agreed with the United States Environmental Protection Agency to commit to working toward the elimination of PFOA, chemicals that breakdown to PFOA, and related higher homologues by 2015. As a result, there has been a shift by some fluorochemical producers to production of C_6-, C_4- and C_3-perfluoroalkylated chemicals. While comprehensive information is lacking about the health effects of these chemicals, toxic effects have been observed for some of them.

6. For some uses, non-fluorinated chemicals such as silicones, aliphatic alcohols and sulfosuccinates have been introduced as alternatives. In other cases particular uses or products are obsolete or could be changed so that they do not require PFOS; example include digital techniques in the photographic industry and the use of mechanical processes for grease-proofing of paper.

7. A comparative assessment of PFOS and possible alternatives with regard to technical, social, economic, environmental, health and safety considerations is a very complex task requiring a large amount of data and other information – more than is normally available. Often the available information about PFOS is much more extensive than the available information about possible alternatives, which may be newly developed substances or formulations claimed to be trade secrets.

8. Furthermore, much of the information on a given alternative is often non-peer-reviewed and may be of relatively low scientific quality. A mechanism may be needed for continually updating information regarding the substitution and hazard properties of alternatives. Such a mechanism would be consistent with subparagraph 1 (b) of Article 9 of the Convention regarding the exchange of information on alternatives to persistent organic pollutants.

9. Available economic data may also be scarce and biased. The information received to date, however, suggests that alternatives are priced comparably to the PFOS-related compounds. Especially for coatings and paints, the non-fluorinated alternatives are cheaper.

10. PFOS and its derivatives are hazardous and, once released to the environment, will stay there forever since no degradation is foreseen. The final deposition site is likely to be the water bodies. Parties shall take appropriate measures to ensure that any PFOS production or use under any specific exemption or acceptable purpose is carried out in a manner that prevents or minimizes human exposure and release into the environment.

11. There is a need for incentives for the development and application of safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for such development. The requirements of the Stockholm Convention that must be implemented in national legislation by all parties to the Convention can serve as an important tool for promoting such incentives.

12. Because of current restrictions governing PFOS, there may be efforts to manufacture and use chemicals that are structurally similar to PFOS but are unregulated. The risks posed by these substances, along with their socio-economic impacts, should be considered in deciding whether and how to regulate their use. Furthermore, the Stockholm Convention obligates Parties with regulatory and assessment schemes to regulate with the aim of preventing the production and use of new chemicals exhibiting POPs characteristics.

13. Increased efforts are needed to study the toxicological and environmental properties of alternatives and to make the resulting data and information public by subjecting it to peer review and publishing it in scientific journals.

14. PFOS and its alternatives are being studied and evaluated in parallel by authorities in many countries. Enhanced international cooperation will save resources and speed up these processes.

I. Introduction, background and objectives

A. History of the proposal to list PFOS in the Stockholm Convention

15. A letter of 14 July 2005 from the Swedish Ministry of the Environment proposed listing PFOS in Annex A to the Convention. A proposal to that end was discussed at the first meeting of the Persistent Organic Pollutants Review Committee in November 2005. [1] The Committee concluded (decision POPRC-1/7) that the information on PFOS presented met the screening criteria specified in Annex D to the Convention. A PFOS risk profile was adopted at the Committee's second meeting, in November 2006, and published on 21 November 2006.[2] A risk management evaluation for PFOS was adopted at the Committee's third meeting, in November 2007, and published on 4 December 2007. [3] Finally, an addendum to the risk management evaluation was adopted at the Committee's fourth meeting, in October 2008, and published on 30 October 2008.[4]

B. Decision at the fourth meeting of the Conference of the Parties

16. At its fourth meeting the Conference of the Parties decided to amend Annex B to list PFOS, its salts and PFOSF.[5] Some acceptable purposes and specified exemptions were agreed upon because of a lack of alternatives for various uses at that time, especially in developing countries and countries with economies in transition.

C. Objective and development of the guidance

17. The objective of this guidance document is to summarize what is currently known about alternatives to PFOS, its salts and PFOSF and to enhance the capacity of developing countries and countries with economies in transition to phase out PFOS, taking into account the need for phase-in times for alternatives for some uses and the fact that for certain uses alternatives may not be currently readily available in all countries.

18. At its sixth meeting, in 2010, the Persistent Organic Pollutants Review Committee endorsed the guidance on alternatives to perfluorooctane sulfonate and its derivatives, on the basis of the draft guidance contained in document UNEP/POPS/POPRC.6/INF/8 as amended during the meeting. At its seventh meeting, the Committee revised the guidance on the basis of comments received from parties and observers. At its eighth meeting in October 2012, the Committee agreed that the title of the guidance should be changed to "guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals".

19. In addition to the present guidance, in response to a request by the Conference of the Parties (COP) to the Stockholm Convention, a technical paper on the identification and assessment of alternatives to the use of PFOS in open applicationswas commissioned in 2012 on the basis of terms of reference developed by the Committee.[6] The information on alternatives to PFOS contained in that document was collected more recently than information contained in the first version of the present guidance. At its eighth meeting, the Committee adopted recommendations on alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications, prepared on the basis of the technical paper, for consideration by the COP. One of the recommendations was that the present guidance be revised to incorporate the information contained in the technical paper.

D. Other information

20. While data on some alternatives listed in the document may be lacking, there is extensive data on others, for instance on PFBA, PFBS, PFHxS, and PFHxA, for which studies are peer reviewed and published in journals. In addition, U.S. EPA has been reviewing substitutes for PFOS, PFOA and other long-chain perfluorinated substances since 2000, and to date, over 150 alternatives of various types have been received and reviewed by U.S.EPA. Similarly, other government agencies have received and reviewed information on alternatives. Recently, a portal has been established to share information on alternatives to perfluorinated chemicals.[7]

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1 UNEP/POPS/POPRC.1/9 and UNEP/POPS/POPRC.1/INF/9.

2 UNEP/POPS/POPRC.2/17/Add.5.

3 UNEP/POPS/POPRC.3/20/Add.5.

4 UNEP/POPS/POPRC.4/15/Add.6.

5 UNEP/POPS/COP.4/38.

6 UNEP/POPS/POPRC.8/INF/17/Rev.1

7 http://www.oecd.org/site/0,3407,en_21571361_44787844_1_1_1_1_1,00.html

21. A new report from the Danish Ministry of Environment entitled “Substitution of PFOS for use in non-decorative hard chrome plating” has been published on Environmental Project 1371, 2011. The report is available on the website: http://www.mst.dk/publikationer/publications/2011/06/978-87-92779-10-6.htm.[8]

22. Studies following guideline (e.g., OECD, OPPTS) protocols under GLP, a central element of which is independent review of the study, have been conducted and provided to regulators as part of registration processes. The FluoroCouncil chemical industry association encourages all users to ask suppliers of alternatives to provide environmental, health and safety information.[9]

II. Characteristics of PFOS and its related chemicals

A. PFOS related chemicals

23. The chemical names and CAS numbers listed in Annex B as PFOS, its salts, and PFOSF are summarized in table 1.

Table 1: Chemical names and CAS numbers listed in Annex B as PFOS, its salts, and PFOSF

PFOS substance	Acronym	CAS no.
Perfluorooctane sulfonic acid	PFOS	1763-23-1
Potassium perfluorooctane sulfonate	PFOSK	2795-39-3
Lithium perfluorooctane sulfonate	PFOSLi	29457-72-5
Ammonium perfluorooctane sulfonate	PFOSNH4	29081-56-9
Diethanolammonium perfluorooctane sulfonate	PFOSDEA	70225-14-8
Perfluorooctane sulfonyl fluoride	PFOSF	307-35-7
Tetraethylammonium perfluorooctane sulfonate	PFOSTEA	56773-42-3
Di(decyl)di(methyl)ammonium perfluorooctane sulfonate	PFOSDDA	2551099-16-8

24. Many PFOS-related chemicals are not specified in Annex B. PFOS-related chemicals are chemicals that contain the structural element PFOS in their molecular structure and are or were produced with PFOSF as starting or intermediate material. These chemicals are covered through the listing of PFOSF. Therefore the present document includes descriptions of alternatives to substances which are not directly listed in the Convention but which nevertheless are covered by it. Some of the most commonly used PFOS-related chemicals are listed in table 2.

25. The proposal by Sweden to list PFOS in the annexes to the Convention specified PFOS and 96 PFOS related chemicals. The United Kingdom’s report from 2004 contains a draft list of 98 compounds that have the potential to degrade to PFOS in the environment.[10] A report from China indicates that 66 PFOS-related chemicals have been identified in a national inventory in China (2009). In 2007 in Denmark, 92 polyfluorinated substances, including 13 PFOS-related ones, were registered as being used in products.[11] In the preliminary list of PFOS, perfluorinated alkyl sulfonates (PFAS), PFOA and related compounds and chemicals that may degrade to PFCA published by the Organization for Economic Cooperation and Development (OECD),[12] many more PFOS-related chemicals were listed. In Canada more than 60 PFOS-related chemicals have been listed.[13]

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8 Information provided by Nordic Institute of Product Sustainability in 2011.

9 Information provided by FluoroCouncil in 2011.

10 Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

11 Jensen, A.A., Poulsen, P.B., Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, 99. Danish Environmental Protection Agency.

12 http://www.oecd.org/ehs/pfc/

13 http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=98B1954A-1
Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2 or C8F17SO3, or C8F17SO2N Moiety

Table 2: Examples of PFOS-related chemicals

Chemical name	Abbreviation	CAS no.
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8
N-Methyl perfluorooctane sulfonamidoethanol	MeFOSE	2448-09-7
N-Methyl perfluorooctane sulfonamidoethyl acrylate	MeFOSEA	25268-77-3
Ammonium bis[2-*N*-ethyl perfluorooctane sulfonamidoethyl] phosphate[14]		30381-98-7
N-Ethyl perfluorooctane sulfonamide (sulfluramid)	EtFOSA	4151-50-2
N-Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2
N-Ethyl perfluorooctane sulfonamidoethyl acrylate	EtFOSEA	432-82-5
Di[*N*-ethyl perfluorooctane sulfonamidoethyl] phosphate	EtFOSEP	67969-69-1
3-[[(Heptadecafluorooctyl)- sulfonyl]amino]-*N*,*N*,*N*-trimethyl-1-propanaminium iodide/perfluorooctyl sulfonyl quaternary ammonium iodide	Fluorotenside-134	1652-63-7
Potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate		2991-51-7
N-Ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide		61660-12-6

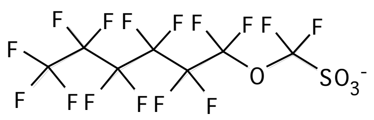
B. Chemicals structurally similar to PFOS

26. Perfluoroalkyl sulfonate (PFAS) is a generic term used to describe any fully fluorinated carbon chain length sulfonic acid, including PFOS and other higher and lower homologues.[15] There are several PFAS and derivatives thereof with shorter or longer alkyl chain lengths than PFOS that are used for applications similar to those for which PFOS is used – in other words as PFOS alternatives. Some examples of PFAS are shown in table 3.

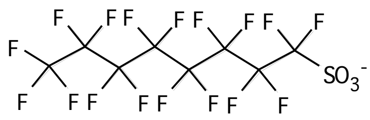
Table 3: Examples of PFAS

Chemical name	Abbreviation	CAS no.
Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	67584-42-3
Perfluorobutane sulfonic acid	PFBS	59933-66-3
Potassium perfluorobutane sulfonate		29420-49-3
Perfluorohexane sulfonic acid	PFHxS	432-50-7
Perfluorodecane sulfonic acid	PFDS	335-77-3
Perfluorodecane sulfonate		67906-42-7

27. Because of the restrictions on PFOS use it is expected that chemicals that are structurally similar to PFOS but are unregulated, such as perfluoro[hexyl methyl ether sulfonate], could be commercialized. The similarity of these substances to PFOS is illustrated by the structure formulas below.



Perfluoro[hexyl methyl ether sulfonate]



Perfluorooctane sulfonate

28. The related perfluoro[hexyl ethyl ether sulfonate] (F-53) is used as mist suppressant in Chinese chrome plating enterprises.

[14] Alternative CAS name: 1-Octanesulfonamide, *N*,*N'*- [phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt.

[15] http://www.oecd.org/document/54/0,3746,en_21571361_44787844_45162486_1_1_1_1,00.html

C. Properties of PFOS-related chemicals

29. The strong carbon-fluorine bond makes the perfluoroalkyl chain present in PFOS extremely stable and nonreactive. PFOS resists even strong acids and high temperatures and is not degradable in the environment. The basic PFOS structure is persistent, and the more complex PFOS-related chemicals listed in table 2 will degrade to the basic PFOS structure during use or presence in the environment.

30. The surfactant properties of PFOS give extremely low surface tension. The perfluorocarbon chain is both oleophobic and hydrophobic; thus it repels water, oil and dirt and insulates electricity. These are considered critical properties of PFOS and perfluorinated surfactants polymers in a number of applications.[16]

31. PFOS as a salt is more hydrophilic and soluble in water. The non-dissociated acid and the sulfonamides are less hydrophilic but more volatile than the salts, and can therefore be transported long distances by air or ocean currents. More details may be found in the PFOS risk profile.[17]

D. Production and consumption of PFOS related substances

32. The company 3M voluntarily phased out PFOS production in 2002 and changed to production of shorter-chain polyfluorinated chemicals (PFCs). Sporadic data on PFOS production exist from national information in Committee documents. For example, in 2003 production of PFOS and PFOSF was initiated in China after production was voluntarily suspended in the United States. In 2006, annual production of PFOSF in China exceeded 200 tonnes, of which about 100 tonnes was exported to other countries, including Brazil and member States of the European Union. In 2003 Germany and Italy produced less than 60 tonnes and less than 22 tonnes of PFOS respectively. The United States in 2006 estimated total use in that country to be less than 8 tonnes a year, and Ireland reported import and use of 10 kilograms of PFOS during 2006. Switzerland gave several estimates for relatively recent use (March 2007) of PFOS, ranging from 230 kilograms to 5 tonnes a year.

33. According to a estimate, global production of PFOSF, the basic chemical for production of PFOS derivatives, was 96,000 tonnes between 1970 and 2002.[18]

III. Alternatives to the use of PFOS

34. At the fourth meeting of the Conference of the Parties, PFOS was listed in Annex B with acceptable purposes and specific exemptions for various applications.

35. PFOS in articles remains, and may continue to be, an issue for all countries that import products containing PFOS, even if PFOS is not manufactured in or imported into that country.

36. The present chapter presents the range of currently available alternatives and describes various uses of PFOS for which chemical and non-chemical alternatives have been suggested, presented or introduced to the market in some countries.

37. The chemical alternatives may provide different levels of functionality than PFOS and may have different toxicity properties. Some alternatives may eliminate PFOS or other fluorinated or chemical alternatives completely. Sometimes, but not always, there is enough information to determine whether they are suitable from both a functionality and environmental health and safety perspective.

38. According to the general guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals,[19] a safer alternative is one that either reduces the potential for harm to human health or the environment or has not been shown to be a potential persistent organic pollutant. The guidance cautions against selecting alternatives to POPs that contain, use or lead to the formation of other chemicals with the characteristics of a persistent organic pollutant or selecting alternatives with hazardous properties such as mutagenicity, carcinogenicity or adverse effects on the reproductive, developmental, endocrine, immune or nervous systems.

39. Non-chemical alternatives to PFOS are also included among potential alternatives. Non-chemical alternatives include alternative industrial processes and innovative practices. It might be that

[16] Information provided by FluoroCouncil in 2011.

[17] UNEP/POPS/POPRC.2/17/Add.5.

[18] Paul, A.G., Jones, K.C., Sweetman, A.J. 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environmental Science and Technology* 43: 386–392.

[19] UNEP/POPS/POPRC.5/10/Add.1.

a particular use or product is obsolete and not essential or that a process or product could be changed so that it does not require the use of PFOS.

40. Some of the major producers of fluorochemicals in Japan, US, and Europe have voluntarily agreed to work toward the elimination of PFOA and C_8-perfluorotelomers, a group of possible alternatives that degrade into PFOA, by 2015. However, the voluntary agreement does not include producers outside these regions and may not prevent other companies from starting or continuing to market long chain PFAS as alternatives to PFOS.[20, 21]

A. Textile (Carpet, Apparel, Leather) impregnation and surface protection

41. Side-chain fluorinated polymers are used extensively by the textile industry and by consumers for the treatment of all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, leather, footwear, rugs, mats, carpets and the like to repel water, oil and dirt (stains).

42. The main PFOS derivatives (normally 2–3% of the fibre weight for textiles but 15% for carpets) previously used for textile and carpet surface treatment applications were the acrylate, methacrylate, adipate and urethane polymers of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE).

43. Examples of well-known trademarked soil and dirt repellents are:

(a) ScotchgardTM (3M);[22]

(b) Capstone® (DuPont);[23]

(c) Products from Daikin, Asahi Glass, Clariant, Rudolf Chemie and others.

44. Before 2000 these were the most important uses of PFOS derivatives. Since it was banned in many countries PFOS has been replaced mainly with shorter-chain analogues and fluorotelomers but also with non-fluorinated chemicals. The trade names have been retained.

45. Analyses of perfluorinated substances in textiles conducted by the Norwegian Institute for Air Research on behalf of the Norwegian Pollution Control Authority have shown very low concentrations or have failed to identify the presence of PFOS. The analyses indicate that perfluorinated acids and telomer alcohols are unintended byproducts and potential degradation products of currently used as alternatives to PFOS in impregnating agents.[24]

46. The alternative polymers for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles are:

(a) Other polyfluorinated compounds with shorter alkyl chain length such as:

(i) Substances based on perfluorobutane sulfonate (PFBS);

(ii) fluorotelomer-based substances, including polymers;

(b) Silicone-based products;[25]

(c) Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins;

(d) Fluorotelomer silicones such as polyfluorooctyl triethoxy silane (1H,1H,2H,2H-perfluorooctyl triethoxy silane, a NanoCover® product) used in a bathroom floor spray product. This and similar substances were banned in Denmark in April 2010 because of toxic effects on mouse lungs.[26]

47. According to the information provided by Argentina in 2011, the leather industry used to use PFOS as water and oil repellent. Currently it has been replaced by perfluorobutane sulfonate.

48. Scotchgard® Protector product produced by 3M (universal spray) containing 1–5% of a perfluorobutane sulfonyl urethane (the identity of the chemical has not been provided by the company)

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20 www.epa.gov/oppt/pfoa/pubs/stewardship/index.html and www.epa.gov/oppt/existing chemicals/pubs/actionsplans/pfcs.html

21 http://www.ec.gc.ca/epe-epa/default.asp?lang=En&n=AE06B51E-1

22 http://solutions.3m.com/wps/portal/3M/en_US/Scotchgard/Home/

23 www.capstone.dupont.com

24 Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

25 High molecular weight siloxanes are normally used.

26 www.mst.dk/Nyheder/Pressemeddelelser/Nanospray.htm

has also been suggested as an alternative for stain-repellent impregnation of textiles, leather and carpets.

49. DuPont has introduced a new brand name, Capstone®, for a series of alternative products for various applications based on short-chain fluorotelomers, mainly involving C_6 chemistry. Other Companies such as Daikin, Asahi and Clariant (and maybe others) have introduced short-chain fluorotelomers as well.

50. Bluestar Silicones markets some silicone-based PFOS alternatives for textile applications under the trade name Advantex®.[27] The technology offers long-lasting water repellence, quick drying, waterproofness and breathability.[28]

51. Rudolph Group, in partnership with Sympatex, has introduced BIONIC-FINISH®ECO as a fluorocarbon-free, water-repellent treatment for textiles.[29] BIONIC-FINISH®ECO is composed of a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers.[30] The exact identity of the chemical has not been provided by the company.

B. Impregnation of packaging (paper/cardboard)

52. Fluorinated chemicals are used in the paper industry to produce waterproof and greaseproof paper. 1.0–1.5% concentration of fluorochemical, based on the dry weight of the fibres, is typically used. Following are the main suppliers of fluorochemicals in the paper industry, with their brand names:

(a) 3M Scotchban®;

(b) Bayer Baysize S®;

(c) Ciba (BASF) Lodyne®;[31]

(d) Clariant Cartafluor®;[32]

(e) DuPont Capstone®;

(f) Daikin Unidyne®;

(g) Asahi Asahigard®;

(h) Solvay Solvera®;

(i) Rudolf Chemie Ruco-guard®.

53. PFOS derivatives have been used both in food contact applications such as plates, food containers, popcorn bags, pizza boxes and wraps and in non-food contact applications such as folding cartons, containers, carbonless forms and masking papers. Paper protection by PFOS derivatives has been achieved by using one of the following:

(a) Mono-, di- or triphosphate esters of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE);

(b) N-Methyl perfluorooctane sulfonamidoethanol acrylate polymers.

54. Before 2000 about 32% of the total use of PFOS in the European Union was for paper coating; the use of PFOS for this purpose is no longer allowed and PFOS has been replaced mainly by other fluorinated chemicals.

55. The known alternative surfactants for impregnation of paper and cardboard for use in packaging are short-chain telomer-based substances and perfluoropolyethers (see 52. d–h), and poly(dimethyl siloxane).

56. Grease-proof paper did exist before PFOS technology was introduced to the market, and other technologies can do the work. In a survey conducted by the Norwegian Food Safety Authority in 2006, it was concluded that no fluorinated substances were used in fast-food packaging in Norway. The

27 High molecular weight siloxanes are normally used.

28 www.advantex-textiles.com/

29 There are still data gaps but some data are available in UNEP/POPS/POPRC.8/INF/17/Rev.1.

30 www.rudolf.de/innovations/hydrophobic-future/bionic-finish/self-organisation.htm

31 www.ciba.com/pf/default.asp?search=1&DApname=lodyne

32 www.paper.clariant.com/businesses/paper/internet.nsf/vw WebPagesByID/65137D7B8419F6EDC12571E0003D5C16

Norwegian paper producer Nordic Paper is using mechanical processes to produce, without using any persistent chemical, extra-dense paper that inhibits leakage of grease through the paper.[33]

C. Cleaning agents, waxes and polishes for cars and floors

57. PFOS derivatives have historically been used as surfactants to lower surface tension and improve wetting and rinse-off in a variety of industrial and household cleaning products such as automobile waxes, alkaline cleaners, denture cleaners and shampoos, floor polish, dishwashing liquids and car wash products. PFOS derivatives have also been used in carpet spot cleaners.

58. A PFOS derivative that was often used in cleaning agents, floor polishes and auto polishes is potassium N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] glycinate (CAS no. 2991-51-7). The concentration of that PFOS derivative in the final product was generally between 0.005% and 0.01% but might have been ten times as high.

59. The possible alternative chemicals identified for use in cleaning agents, waxes and floor polishes are:

(a) Short chain telomer-based surfactants and polymers;[34]

(b) Various C4-perfluorinated compounds: Novec® (3M), for commercial and industrial cleaning, contains methyl nonafluorobutyl ether (CAS no. 163702-07-6) and methyl nonafluoroisobutyl ether (CAS no. 163702-08-7);

(c) Fluorinated polyethers: PolyFox® (OMNOVA Solutions Inc.), a line of fluorosurfactants that are polymers with a molecular weight greater than 1,000 based on ether links and with C2F5 or CF3 as the starting material.

60. A shift to softer waxes that are more biodegradable or entirely biodegradable may completely eliminate the need for persistent polyfluorinated compounds. In these products, the fluorinated surfactants are replaced with non-ionic or anionic surfactants, which have good wetting properties.

D. Surface coating, paint and varnish

61. PFOS derivatives have had several uses in coating, paint and varnishes to reduce surface tension – for example, for substrate wetting, for levelling, as dispersing agents and for improving gloss and antistatic properties. PFOS derivatives can be used as additives in dyes and ink, as pigment grinding aids and as agents to combat pigment flotation problems. The concentrations used were below 0.01% (w/w).

62. The possible alternatives identified for use in paints and varnishes are surfactants based on the following:

(a) Short chain fluorotelomer-based surfactants (e.g. Capstone® products);[35]

(b) C4-compounds based on perfluorobutane sulfonate, especially in the area of electronic coating;

(c) Fluorinated polyethers (PolyFox®);

(d) Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water, which is used as an alternative in wood primers and printing inks;

(e) Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd®);

(f) Propylated naphthalenes and propylated biphenyls, which can be used as water repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications;

(g) Fatty alcohol polyglycol ether sulfate, sometimes together with a sulfosuccinate.

63. Information from suppliers in the paint and varnish industry suggests that fluorosurfactants are in general much more expensive than other alternative surfactants.[36] They are therefore used in paint

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[33] Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

[34] Survey, screening and analyses of PFCs in consumer products, KLIF TA-2578/2009 (2009) http://www.miljodirektoratet.no/old/klif/publikasjoner/2578/ta2578.pdf.

[35] Perfluorocarboxylic Acid Content in 116 Articles of Commerce, US EPA (2009) http://www.oecd.org/env/48125746.pdf.

and varnishes only in situations where very low surface tension is desired and no other (non-fluorinated) alternatives can achieve it (e.g., in products where an extremely smooth surface is desired).

E. Oil production and mining

64. PFOS derivatives may be used as surfactants in the oil and mining industry to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, as jet fuel and hydrocarbon solvents and to enhance the amount of recovery of metals from the ores in copper and gold mines. According to information submitted by China at the fourth meeting of the Conference of the Parties, at the time PFOS was still used as a surfactant in old oil fields in China to recover oil trapped in small pores between rock particles. At the meeting, several representatives of other countries questioned this use of PFOS, saying that oil production and mining took place in their countries without the use of PFOS, which indicated that there were alternative processes that did not require PFOS.

65. According to information from the 2006 OECD survey, tetraethylammonium perfluorooctane sulfonate and potassium perfluorooctane sulfonate were used in the mining industry in member countries as suppressing agents in an annual combined volume of up to 50 tonnes.[37]

66. Current information about alternatives in the oil and mining industries is scarce. 3M has, according to OECD, introduced PFBS as an alternative. Other perfluoro-compounds patented (United States patent 20030153780) for uses in oil recovery are perfluoroalkyl-substituted amines, acids, amino acids and thioether acids.[38]

F. Photographic industry

67. In the photographic industry PFOS-related substances (tetraethylammonium perfluorooctane sulfonate and perfluorooctyl sulfonamidopropyl quaternary ammonium iodide) have been used in manufacturing film, paper and plates. These PFOS-related compounds function as dirt rejecters and friction control agents and to reduce surface tension and static electricity. Imaging materials that are very sensitive to light (e.g., high-speed films) benefit particularly from these properties. The concentration of PFOS-related substances in coatings in films, paper and plates is in the range of 0.1–0.8 $\mu g/cm^2$.

68. As the spread of digital cameras has reduced film use, the use of PFOS in this area is not expected to grow. World consumption of PFOS for colour film production fell from 23 tonnes in 2000 to 8 tonnes in 2004. Current annual consumption in the European Union’s photographic industry is 1 tonne. According to the industry, the estimated annual cost of this 83% reduction has been €20million to €40 million.

69. According to the 2006 OECD survey, up to 20 tonnes of lithium perfluorooctane sulfonate and perfluorooctane sulfonic acid were, at the time of the survey, used annually in the photographic industry as anti-reflective agents.[39]

70. PFOS is still used (probably in small quantities) in X-ray film for photo imaging for medical and industrial uses (inspection by non-destructive testing). It is also used in film for other industries, such as the movie industry, as alternatives are claimed not to be of comparably high quality. Use of PFOS in industrial photographic coatings is exempt from the PFOS ban in the European Union. In Canada, the use, sale, offer for sale and import of photographic films, papers or printing plates containing PFOS, its salts or its precursors is permitted.

71. PFOS-related compounds have also been used in developers for photographic film. According to EU Directive 2006/122/EC this application is now banned. Japan’s photographic industry has reported that PFOS is no longer used for photographic processing in Europe, Japan, North America or elsewhere. Since photographic processing solutions using PFOS were highly sophisticated products, they were produced and supplied by a limited number of manufacturers, which have stopped using PFOS for their photographic processing products.

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[36] Poulsen, P.B., Jensen. A.A., Wallström, E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project no. 1013. Danish Environmental Protection Agency. www2.mst.dk/Udgiv/publications/2005/87-7614-668-5/pdf/87-7614-669-3.pdf

[37] Organization for Economic Cooperation and Development. 2006. Results of the 2006 OECD Survey on Production and Use of PFOS, PFAS, PFOA, PFCA, Their Related Substances and Products/Mixtures Containing These Substances. ENV/JM/MONO(2006)36. Available at www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en

[38] Information from the United States Environmental Protection Agency, 2009.

[39] www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en

72. The possible alternatives identified for the photographic industry are:

(a) Digital techniques;

(b) Telomer-based products of various perfluoroalkyl chain length;

(c) C3- and C4-perfluorinated compounds;

(d) Hydrocarbon surfactants;

(e) Silicone products.[40]

73. Desirable properties for chemical alternatives in these uses include dynamic surface tension capability, static inhibition, solubility, photo-inactivity and stability when subjected to heat and chemicals.

G. Electrical and electronic parts

74. Electrical and electronic equipment often requires hundreds of parts and thousands of processes. PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, radar systems and the like. The PFOS-related compounds are used as process chemicals, and the final products are considered as mostly PFOS-free.[41] No information about effects on the environment or human health, or about the level of PFOS in electronic waste, is available. Intermediate transfer belts of colour copiers and printers contain up to 100 ppm of PFOS, while an additive used in producing PFA (perfluoroalkoxy) rollers contains 8×10^{-4} ppm PFOS. Industry groups reported that alternatives are currently not available for those applications.

H. Semiconductor industry

75. PFOS reduces the surface tension and reflectivity of etching solutions, properties that are important for precise photolithography in the semiconductor industry (photo resists and photo masks).[42] Small amounts of PFOS-based compounds are required during the following critical photolithography applications in manufacturing semiconductor chips:[43]

(a) Ultra-fine patterning/photo res[is]ts as photo-acid generators and surfactants;

(b) Anti-reflective coatings as uniquely performing surfactants.

76. The exact PFOS derivative used is not publicly known.

77. These applications are crucial for achieving the accuracy and precision required to manufacture miniaturized high-performance semiconductor chips. The annual use of PFOS in the European Union’s semiconductor industry before 2000 was 470 kilograms, with emissions of 54 kilograms. Due to the European industry’s successful efforts to reduce uses of PFOS, the annual use in 2010 for the remaining critical uses was 10 kilograms with emissions of less than 0.5 of a kilogram.

78. According to the industry no alternatives are currently available that would allow for the comprehensive substitution of PFOS in these particular applications, which have been exempted from restrictions on PFOS use. The World Semiconductor Council, an industry body, was committed to ending non-critical uses of PFOS in member countries of the United Nations Economic Commission for Europe by May 2007 and globally in May 2009 The World Semiconductor Council (WSC) consisting of the Semiconductor Industry Associations in China, Chinese Taipei, Europe, Japan, Korea and the United States agreed to this voluntary agreement on PFOS in 2006 and subsequently implemented that agreement.

79. The Japanese semiconductor industry has been using less than 5 kilograms of PFOS annually for the etching of high-frequency compound semiconductors and piezoelectric ceramic filters. Alternative methods yielding comparable quality are not currently available, and more research and development are needed to achieve that quality. According to a submission from Japan, alternative methods are expected to be available in 2014.[44]

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40 There are cosiderable datagaps of siloxane compounds used on the market for photographic applications, see reference UNEP/POPS/POPRC.8/INF/17/Rev.1.

41 UNEP-POPS-GUID-NIP-2012-PFOS-Inventory.En; UNEP-POPS-GUID-NIP-2012-BATBEPPFOS.En

42 Photo masks are optically transparent fused quartz blanks imprinted with a pattern defined with chrome metal and are the templates used to inscribe the circuit pattern into the photo resist.

43 Information provided by the European Semiconductor Industry Association.

44 UNEP/POPS/POPRC.4/INF/17/Rev.1.

80. According to information submitted by the Chinese delegation to the fourth meeting of the Conference of the Parties, the semiconductor industry in China uses 30–40 kilograms of PFOS yearly for photo resists, as an anti-reflective coating, as a de-gluing agent and as a developing agent, and in 2007 industry sales were ¥100 billion.[45] The WSC has announced publicly in 2011 that the global semiconductor industry has successfully eliminated all non-critical uses of PFOS and identified substitutes for most other uses, although continued use of very small quantities of PFOS remains critical in a few remaining processes (the critical applications in manufacturing semiconductor chips such as photo resist and anti-reflective coatings for semiconductors). The remaining critical uses of PFOS are limited and highly controlled, and emissions of PFOS by the entire global semiconductor industry have been reduced to approximately 6 kg/year. The acceptable purpose exemptions under the Stockholm Convention are still required. In 2011 the WSC also announced that, the semiconductor industry has reduced global emissions of PFOS from semiconductor use to approximately 6kg/year which represents a 99% reduction from semiconductor emissions in 2005. These emissions will continue to reduce as technology and feasibility permit replacement of critical uses.

81. New photolithography technologies use less photo resist per wafer than older technologies, and the new photo resist formulations contain much lower concentrations of PFOS. Thus, the total use of PFOS is decreasing, lowering the total amount of releases. In 2002, effluent releases for these critical uses for the whole of Europe totalled an estimated 43 kilograms of PFOS. As PFOS does not break down, this represents an ongoing accumulative load to the environment. PFOS has been found to be the major constituent in semiconductor manufacturing plant wastewaters along with other PFCs and perfluoroalkyl carboxylates including PFOA and PFDA.[46]

82. The cost of developing a new photo-resist system is estimated to be US$700 million (0.3 % of annual sales) for an industry which had global sales of US$248 billion in 2006. This indicates that cost is not a barrier to develop a new photo-resist system.

83. PFOS was used to produce developers and edge bead removers. Substitutes do exist for these non-critical uses, and the semiconductor industry has phased out these uses. In the photolithography industry, it is considered that few alternatives are available that would allow for the comprehensive substitution of PFOS in critical applications. Thus the new photolithography technologies, which in detail are trade secrets, use less photoresist per wafer, and the new photoresist formulations contain much lower concentrations of PFOS. Non-critical uses of PFOS are as edge bead removers, de-gluing agents and developing agents. Substitution requires varying lengths of time. According to the industry, smooth substitution often requires more than 10 years, and substitution without approval from customers tends to halt the latter’s production lines. Customers expect alternatives to perform comparably to PFOS-containing items.

84. There may be one additional specialized application for which, according to industry sources, there is currently no substitute for PFOS: use in liquid etchant in the photo ask rendering process. For photo mask etching with strong acids non-fluorosurfactants are not stable enough, and shorter-chain fluorosurfactants do not have sufficiently low surface tensions.

I. Aviation hydraulic fluids

85. Hydraulic oils with a potassium perfluorooctane sulfonate content of about 0.1% have been used in civil and military airplanes since the 1970s (United States patent 3679587 dates from 1972) to prevent evaporation, fires and corrosion. The total global market for fluorinated compounds in aircraft hydraulic fluids is about 2 tonnes per year. Annual PFOS consumption in the European Union for this use was about 730 kilograms/year in 2009.[47]

86. There is uncertainty about alternative substances in this area. Aviation hydraulic fluids without fluorinated chemicals but based on, for example, phosphate esters exist,[48] and fluorinated chemicals other than PFOS can be used.

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[45] UNEP-POPS-POPRC-SUB-F08-PFOS-ADIN-CHI.English.pdf

[46] Lin AY, Panchangam SC, Lo CC (2009). The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers.Environ Pollut. 2009 Apr;157(4):1365-72. doi: 10.1016/j.envpol.2008.11.033. Epub 2008 Dec 30.

[47] Dorian Carloni “Perfluorooctane Sulfonate (PFOS) ; Production and Use: Past and Current Evidence”, UNIDO (2009) http://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/POPs/DC_Perfluorooctane%20Sulfonate%20Report.PDF

[48] www.freepatentsonline.com/6319423.html and www.freepatentsonline.com/WO2006138081.html

87. An anti-erosion agent added to the hydraulic fluid contains an unidentified residual organic fluorochemical which is most likely a by-product of the manufacturing process. It is possible that this residual substance could be PFOS. This residual substance is only present at very low levels (a few parts per million) and is only formed in an environment with high pressure and fluorine . The presence of this substance could be considered an "unintentional trace contaminants".

J. Pesticides

88. *N*-Ethyl perfluorooctane sulfonamide (EtFOSA; sulfluramid; CAS no. 4151-50-2) is both a surfactant and a pesticide used in tropical areas against termites, cockroaches and other insects and in Brazil for control of leaf-cutting ants from the species of *Atta spp.* and *Acromyrmex spp*.

89. According to information from the 2006 OECD survey sulfluramid was used in insecticides at a concentration of 0.01-0.1% at an annual volume of up to 17 tonnes.

90. Fluorosurfactants may also be used as "inert" surfactants (enhancers used in pesticide formulations but not constituting active ingredients) in pesticide products. The two PFOS-related substances potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS no. 2991-51-7) and 3-[[(heptadecafluorooctyl)sulfonyl]amino]-*N*,*N*,*N*-trimethyl 1-propanaminium iodide (CAS no. 1652-63-7) have been approved in pesticide formulations in the United States in the past.[49] However, 3-[[(heptadecafluorooctyl)sulfonyl]amino]-N,N,N-trimethyl 1-propanaminium iodide (CAS no. 1652-63-7) is currently only approved for non-food use and potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS no. 2991-51-7) is no longer permitted.[50,51] Both chemicals have other uses, for example as cleaning agents. PFOS derivatives were used in pesticides because they were considered rather inert and non-toxic.

91. PFOS is no longer used to manufacture ant bait or insecticides against beetles and ants in the European Union, and the United States Environmental Protection Agency cancelled the registration of sulfluramid in May 2008.[52] According to information submitted to the secretariat of the Stockholm Convention, sulfluramid had been used for pest control (to control cockroaches, white ants and fire ants) in China, and sulfluramid is used in Brazil in more than 95% of baits for the control of leaf-cutting ants, although the amount of PFOS used was not reported. Since 10% of sulfluramid is degraded to PFOS, its use represents a direct release of PFOS to the environment.[53,54]

92. According to the Brazilian delegation, the use of sulfluramid in Brazil prevents damage corresponding to losses of up to 14.5 % of trees per hectare. Other agricultural products likely to suffer costly losses are soybean and maize. Also, the per-hectare capacity to support livestock is likely to decrease if forage for grazing is reduced by ants.[55]

93. Currently, the active ingredients registered in Brazil for producing bait to control leaf-cutting ants are sulfluramid, fipronil and chlorpyrifos. The latter two, however, are considered more acutely toxic to humans and the environment than sulfluramid. Furthermore, the effectiveness of these substances has been questioned; thus new alternatives are being studied in Brazil. According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose

94. In the EU, PFOS-related substances are not used in the manufacture of pesticides.[56] Ant baits containing S-methoprene and pyriproxifen are registered in New Zealand for the control of exotic ants by aerial and ground applications.[57]

95. There are many differences between leaf-cutting ants and exotic ants (urban ants), including in alimentary behaviour. Such differences explain why certain active ingredients are effective for controlling urban ants and not for controlling leaf-cutting ants. Fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone and methoprene had been tested for leaf-cutting ants, but they were not effective. An adequate insecticide used to formulate bait

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49 www.fluoridealert.org/pesticides/pfos.pfoas-page.htm

50 http://iaspub.epa.gov/apex/pesticides

51 Federal Register: June 24, 1998 (Volume 63, Number 121), Notices, Page 34384-34390.

52 www.epa.gov/fedrgstr/EPA-PEST/2008/May/Day-16/p10919.htm.

53 UNEP/POPS/POPRC.3/20/Add.5.

54 http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7100

55 Oficio Oficio DFIA/SDA/MAPA nº 123/2008 from Ministry of Agriculture, Livestock and Food Supply, Animal and Plant Protection Secretariat Agriculture Inputs Inspection Department.

56 http://archive.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf

57 Environmental Risk Management Authority of New Zealand (ERMA NZ) (2007), Decision, 2007-11-11.

for the control of leaf-cutting ants should be lethal at low concentrations, act by ingestion and present a delayed toxic action. Additionally, it should be odorless and non-repellent, so as to be dispersed by trophallaxis to most workers in the colony. Since 1958, over 7,500 chemical compounds for ant control have been studied in many countries. Fewer than 1% of those 7,500 compounds have shown promise.[58]

96. Leaf-cutter ants have mechanical and chemical defenses that help them to counterbalance the effect of some control measures. Exocrine glands and symbiotic bacteria are the main sources of antimicrobials in leaf-cutter ants, and are used to counter biological control agents. Studying the adaptation mechanisms of leaf-cutter ants is recommended to improve effectiveness of strategies for their ecological management. However biological control can be effective under some conditions. In laboratory studies, the entomopathogenic *Metarrhizium anisopliae* can cause the decline and ultimate death of small colonies and recent research indicates that the entomopathogenic fungi *Beauveria bassiana* and *Aspergillus ochraceus* both show a high degree of control, causing 50% mortality within 4-5 days.[59, 60] Effective natural products include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata*.[61] Further research is required to verify the effectiveness of these interventions under field conditions. Several mechanical, cultural, biological and chemical methods have been studied as early as the 50s for controlling leaf-cutting ants. The management of culture by using resistant plants toxic plants, and the applied biological management, by manipulating predators, parasitoids and micro-organisms, have rendered unsatisfactory and inconsistent results, and have offered no indication of any technical, economic, or operational viability.[62]

K. Medical devices

97. Video endoscopes are used to examine and treat patients at hospitals. Around 70% of the video endoscopes used worldwide, or about 200,000 endoscopes, contain a charge-coupled device (CCD, technology for capturing digital images) colour filter that contains a small amount (150 ng) of PFOS. According to a submission from the Japanese delegation, repairing such video endoscopes requires a CCD colour filter containing PFOS.

98. It is technically possible to produce PFOS-free CCD filters for use in new equipment. There are, however, 200,000 existing endoscopes that use PFOS-containing filters. Gradual phase-out of existing endoscopes will permit the use of PFOS-free equipment.

99. PFOS is also used as an effective dispersant when contrast agents are incorporated into an ethylene tetrafluoroethylene (ETFE) copolymer layer. PFOS plays an important role in radio-opaque ETFE production, allowing the achievement of the levels of accuracy and precision required in medical devices (e.g., radio-opaque catheters, such as catheters for angiography and in-dwelling needle catheters).

100. Since about 2000, when the harmful environmental effects of PFOS were identified, manufacturers of radio-opaque ETFE have been working with chemical materials suppliers to find alternatives. The 2006 OECD survey identified the use of PFBS as a surfactant in coating products. In some cases this substance can be used as a dispersant for inorganic contrast agent when it is mixed into ETFE.

101. Medical fabrics, such as woven or nonwoven surgical drapes and gowns are treated with side-chain fluorinated polymers (such as PFAS- or fluorotelomer-based (meth)acrylate polymers and polyurethanes) to modify the surfaces, in order to impart water-, oil-, and staining resistance.

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[58] UNEP-POPS-POPRC-SUB-F08-PFOS-LEAF-N1.English.

[59] D.B. Jaccoud, W.O.H. Hughes and C.W. Jackson, *The epizootiology of a Metarhizium infection in mini-nests of the leaf-cutting ant Atta sexdens rubropilosa*, 1999, ENTOMOLOGIA EXPERIMENTALIS ET APPLICATA, Volume 93, Number 1, 51-61, DOI: 10.1023/A:1003830625680.

[60] Myriam M. R. Ribeiro,1 Karina D. Amaral, Vanessa E. Seide, Bressane M. R. Souza,1 Terezinha M. C. Della Lucia, Maria Catarina M. Kasuya,2 and Danival J. de Souza, *Diversity of Fungi Associated with Atta bisphaerica (Hymenoptera: Formicidae): The Activity of Aspergillus ochraceus and Beauveria bassiana,* Psyche Volume 2012, 2012, Article ID 389806, 6 pages, doi:10.1155/2012/389806.

[61] Maique W. Biavatti*, I; Rosângela WesterlonI; Paulo C. Vieira; M. Fátima G. F. da Silva; João B. Fernandes; M. Fernanda G. V. Peñaflor; Odair C. Bueno; Javier Ellena, *Leaf-cutting ants toxicity of limonexic acid and degraded limonoids from Raulinoa echinata.* X-ray structure of epoxy-fraxinellone, Journal of the Brazilian Chemical Society *Print version* ISSN 0103-5053. Chem. Soc. vol.16 no.6b São Paulo Nov./Dec. 2005.

[62] D.B. Jaccoud, W.O.H. Hughes and C.W. Jackson, *The epizootiology of a Metarhizium infection in mini-nests of the leaf-cutting ant Atta sexdens rubropilosa*, 1999, ENTOMOLOGIA EXPERIMENTALIS ET APPLICATA, Volume 93, Number 1, 51-61, DOI: 10.1023/A:1003830625680.

L. Metal plating

102. PFOS is used as a surfactant, wetting agent and mist suppressing agent for chrome plating to create a protective foam and decrease aerosol emissions and improve the work environment. It was previously used for both decorative chrome plating and hard chrome plating processes, but new technology using chromium-III instead of chromium-VI for certain decorative chrome plating has made PFOS use in decorative chrome plating obsolete. Chromium-III does not work for hard chrome plating, however. The use of PFOS as a wetting agent for hard chromium plating is considered listed as an acceptable purpose and specific exemption.

103. In hard chrome plating PFOS works by lowering the surface tension of the plating solution and forming a single foamy film barrier of a thickness of about 6 nanometres on the surface of the chromic acid bath, which maintains its aerosol (fog) formation, thus reducing airborne loss of chromium-VI from the bath and decreasing exposure of workers to this carcinogenic agent.

104. The PFOS derivative most frequently used in hard chrome plating is the quaternary ammonium salt tetraethylammonium perfluorooctane sulfonate (sold under trade names such as Fluorotenside-248 and SurTec 960), typically in a 5–10% solution. The potassium, lithium, diethanolamine and ammonium salts of perfluorooctane sulfonic acid may also be used.

105. In Europe, and also in Canada ATOTECH markets Fumetrol® 140 with PFOS and Fumetrol® 21 without PFOS but with the fluorotelomer derivatives 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (CAS no. 27619-97-2).Other names are 6:2-Fluorotelomer sulfonate (6:2 FTS) or (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate. There is some uncertainty about its efficacy although some trials show equivalent results with 6:2FTS as with PFOS.[63] There is some uncertainty about its efficacy and suitability for certain metal finishing applications. For example, in the aerospace industry, Fumetrol 21 LF was tested to the same chromic acid anodize qualification standards as Fumetrol 140. This included salt spray, paint adhesion, coating weights, bend fracture SEM analysis, and other tests. The addition of Fumetrol 21 LF to the chromic acid anodize bath interfered with coating weight development. This resulted in the inability to meet specification requirements for coating weight and corrosion resistance performance.

106. Some fluor-free alternatives such as TIB Suract CR-H are also used on the market.[64] An economic assessment of the non-PFOS alternatives depends on:

(a) The price of the chemicals and or physical alternatives;

(b) The amount needed during use;

(c) The expenses during substitution;

(d) Expenses to possible continuous addition of chemicals;

(e) Expenses related to possible break down of a continuous addition system, due to problems related to non-sufficient or excess additions of chemicals.

The price of the chemicals

107. In a Danish study conducted 2011, suppliers of PFOS and non-PFOS alternatives were contacted in order to learn more about the price of the chemicals. However, only price information was received about the price for a few of the chemicals and mostly for the PFOS products.

108. The information received in this Danish study from the suppliers, suggests that the price of the PFOS products used as mist suppressant for non-decorative hard chrome plating is around 100 to 200 DKK (13 EUR to 27 EUR) per kilo/liter. The price is dependent on the concentration of PFOS in the chemical. The cheaper products contain about 2-3 % PFOS whereas the more expensive products contains 3-7 % PFOS.

109. In comparison one of the alternatives was found to cost 120 DKK (16 EUR) per kilo/liter. The price is not fully comparable as no information was received on the amounts to be used compared to a PFOS product. However, the supplier informed that the product was cheaper than using PFOS. Other information about the price of the non-PFOS alternatives was sparse. One supplier informed that their non-PFOS alternative is more expensive than PFOS (but not how much more expensive).

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[63] Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

[64] Personal communication from Pia B. Poulsen, FORCE Technology, August 2010.

110. In conclusion, the economic assessment of the non-PFOS alternatives based on the price alone is inconclusive. Some alternatives may be cheaper and some may be more expensive.

111. Non-fluorinated alternatives for hard chrome plating are available on the European market but are very new, and some are still being tested. These alternatives (whose chemical description and CAS numbers have not been released by the private sector) appear functional with some slight process changes including stirring the chromium bath.

112. During the electroplating process, the protective foam layer that prevents misting of chromic acid is eventually broken down. Then there is a need to refill the bath with additional wetting and mist suppressant agent to maintain a stable protective foam layer over the chrome bath, and after about 7 months only about 1% of the original content is left.[65] Thus, the bath must be refilled with PFOS once the foam layer is insufficient to withhold the Cr-VI aerosols. Alternatives to the PFOS derivatives are considered to be less stable and durable in the chrome bath than PFOS since they may not reach the necessary surface tension and additionally they degrade further through oxidation which is not the case for PFOS. This is due to the extreme persistence of PFOS which is considered as one of the most stable chemicals in fluoro chemistry.

113. Discussions with stakeholders in the chrome plating industry in Denmark has revealed that they have not received information about the content of PFOS and the hazards of fluorosurfactants, which have been marketed as safe products.[66] Thus the incentive to introduce alternative substances and processes has been low. Because fluorosurfactants are not classified as dangerous, this use in Denmark is not reported to the National Product Registry, and its extent is not known to the authorities.[67]

114. When the chrome plating solution is spent, the bath is exhausted and the plating solution liquid must be disposed of. However it must be taken into account that, due to the high ability of PFOS to absorb to the surface of most materials and "memory effect", PFOS can be found in the wastewater stream of electroplating plants for months (or, in some cases, more than a year) after being substituted. Ion exchangers, washing water from exhausters and every contact surface must be purified or exchanged as well as the electrolyte liquid itself.[68] The solution is sent to a chemical waste water plant, where the chromium is precipitated as chromium (III) hydroxide. The resulting dewatered sludge is sent to specially prepared landfills, engineered to prevent leakage, where the sludge is stored.[69]

115. The sludge is sometimes used as a fertilizer for agricultural soil which can result in broad scale contamination of agricultural fields with PFOS and provide a major emission source to food and water.[70] A great part of the PFC used in this industry therefore probably ends up in the environment. That would seem to be confirmed by the recent discovery of high levels of PFOS in agricultural soils in the United States and Germany.[71] In 2009, the German national metal plating association (ZVO) stated that in Germany 20% of PFC is lost to the environment.[72]

116. In the European Union the annual PFOS use for chrome plating was about 10 tonnes in 2003 but has declined recently. According to data from the European Commission (2010) the total use in the European Union today is estimated to be around 4 tonnes.[73]

117. China reported that its chrome plating industry uses 25 tonnes of PFOS a year. The PFOS-containing mist suppressants used in China are FC-80 (CAS no. 2795-39-3 – PFOS potassium salt) and FC-248 (CAS no. 56773-42-3 – PFOS tetraethyl ammonium salt). The industry turnover is ¥30

65 Personal communication from Carsten Ree Jørgensen, CEO, Nichro, 2009.

66 Personal communication from Per Møller, Technical University of Denmark, 16 March 2009.

67 Personal communication from Frank Jensen, Danish Environmental Protection Agency, 17 March 2009.

68 Breidenbach H. 2009. Substitution von perfluorierten Netzmitteln in Chrombädern 2009 Oberflächen Polysurfaces No. 6/2009. http://www.polymedia.ch/htdocs/Files/Polysurfaces/OP-archives/2009/OP_2009-06.pdf

69 IPPC BREF BAT for the Surface Treatment of Metals and Plastics European Commission, 2006.

70 Krofges P, Skutlarek D, Farber H, Baitinger C, Godeke I, Weber R., PFOS/PFOA Contaminated Megasites In Germany Polluting The Drinking Water Supply Of Millions Of People Organohalogen Compounds Vol. 69 (2007).

71 Renner R. 2009. EPA finds record PFOS, PFOA levels in Alabama grazing fields. *Environmental Science and Technology* 43: 1246–1247.

72 Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

73 European Commission. 29 January 2010. Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks.

billion. A phase-out without an effective alternative could worsen the health of 100,000 Chinese workers through exposure to Cr-VI, according to Chinese authorities. . In China the available PFOS alternatives used for chrome plating are F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate, CAS no. 756426-58-1), F-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate, CAS RN 73606-19-6) and Fumetrol® 21(1H,1H,2H,2H-perfluorooctane sulfonic acid).[74]

118. Canada reports having imported an estimated 3 metric tonnes of PFOS from the United States in 2004 for use in metal plating. Since the implementation of the *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* in 2008, the quantities imported into Canada for this use have decreased significantly. The use of PFOS containing substances in this application will be prohibited after May 2013. Of the suppliers of fume suppressants to the metal finishing (chromium plating/anodizing) industry in Canada, many report that PFOS-free fume suppressants are now already in use. Atotech Canada reports that all Canadian accounts are now using PFOS free fume suppressants or other control technologies. Other Canadian suppliers report approximately an 85 – 90% change to PFOS free fume suppressants.[75] France reports having used 200 kilograms of PFOS for metal plating in 2006. All these figures are for chromium plating, including decorative plating. A comprehensive report by the United States Environmental Protection Agency on the detectable levels of PFOS in the effluent of decorative chromium electroplating facilities is available.[76]

119. The German national metal plating association (ZVO) describes the availability of PFOS-free alternative products from 10 German suppliers.[77] While information is lacking about the exact identity of these chemical compounds, three of them were fluorinated chemicals and seven were fluorine-free. The non-fluorinated alternatives were not stable enough in the hard chrome plating bath. It is stated that all 10 products could be used for decorative chrome plating, for which alternative Cr-III processes seem to exist already. Alternative surfactants for this process are being studied at the University of Wuppertal, Germany.[78] One possible non-fluorinated surfactant alternative for decorative plating may be Enthone® (ethoxylated oleyl amine, CAS no. 26635-93-8).

120. The Norwegian association of electroplaters (Norsk Galvanoteknisk Landsforening, or NGLF) has reported that its suppliers no longer provide PFOS wetting/anti-mist agent for chrome plating but instead provide PFOS-free tensides. NGLF considers the performance of those alternatives to be insufficient, however, and is developing better alternatives to PFOS and alternative technologies to solve the problem of airborne loss of hexavalent chromium from baths. NGLF has estimated the cost of replacing Cr-VI in plating baths with Cr-III to be approximately NKR100,000 (US$15,000–16,000) per bath. NGLF, however, reports that the industry has already started to phase out the use of PFOS-containing wetting/anti-mist agent by using the Cr-III process instead of the Cr-VI process where possible.[79]

121. In Japan the use of PFOS in hard chrome plating has also been discontinued.[80]

122. The use of control devices, such as Composite Mesh Pads (CMP) or Packed Bed Scrubbers (PBS), to catch aerosols from chromium plating baths offers an alternative to the use of PFOS. CMP operate at over 99% efficiency on 1 micron sized particles while PBS operate with over 98% efficiency removal of chrome VI aerosols. CMP are currently considered to be maximum achievable control technology of chrome VI aerosols, but these installations cost more than current operations. Closed tanks with increased ventilation have been suggested as alternative solutions to CMP and PBS for applications where use of chromium-III is not yet possible. However, such systems need further improvement to be as effective as control devices in getting rid of chromium emissions. There is some concern that increased ventilation will also result in increased energy consumption and loss of some

74 Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

75 Personal Communication P. J. Paine, Environment Canada, July 2012.

76 www.epa.gov/r5water/npdestek/pdf/pfoschromeplaterstudypdf_final.pdf

77 Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

78 Personal communication from Jutta Hildenbrand, University ofWuppertal, 15 October 2009.

79 Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

80 Poulsen et. al, Substitution of PFOS for use in nondecorative hard chrome plating (2011), Danish Ministry of Environment, p 32. http://www2.mst.dk/udgiv/publications/2011/06/978-87-92779-10-6.pdf.

chromium from baths.[81] Other methods such as using physical covers (netting, balls) for baths to diminish hydrogen burst and reduce misting currently do not work but should be further investigated.[82]

123. Besides chrome plating, fluorinated surfactants (including PFOS) are also used in other metal plating applications,[83] for example:

(a) Agents to prevent haziness of plated copper by regulating foam and improving its stability;

(b) Non-foaming surfactants in nickel-plating baths to reduce surface tension;

(c) Agents added to tin-plating baths to ensure that plating has uniform thickness;

(d) Agents to impart a positive charge to fluoropolymer particles and to aid electroplating of polymers (e.g. PTFE) onto steel for surface protection.

124. No assessments or reports have been made regarding alternatives to uses listed above.

M. Fire-fighting foams

125. Fire-fighting foams with fluorosurfactants are very effective for extinguishing liquid fuel fires at airports and oil refineries and storage facilities. However, they also represent a direct release of PFOS to the environment. Types of fire-fighting foams include:

(a) Fluoro-protein foams used for hydrocarbon storage tank protection and marine applications;

(b) Aqueous film-forming foams (AFFF) developed in the 1960s and used for aviation, marine and shallow spill fires;

(c) Film-forming fluoroprotein foams (FFFP) used for aviation and shallow spill fires;

(d) Alcohol-resistant aqueous film-forming foams (AR-AFFF), which are multi-purpose foams;

(e) Alcohol-resistant film-forming fluoroprotein foams (AR-FFFP), which also are multi-purpose foams; developed in the 1970s;

126. Normally, a mixture of fluorinated surfactant and a hydrocarbon-based surfactant is used in AFFF, as this combination is more cost-effective and performs better than either surfactant separately. The concentration of perfluorinated compounds in fire-fighting foams is about 0.9–1.5%.[84]

127. The fluorinated surfactant used in AFFF forms an aqueous film covering the surface of oil and is used for stopping fires at chemical plants, fuel storage facilities, airports, underground parking facilities and tunnels. A PFOS-related compound used in the past was 3-[[(Heptadecafluorooctyl)-sulfonyl]amino]-*N*,*N*,*N*-trimethyl-1-propanaminium iodide.

128. Today most fire-fighting foams are manufactured with fluorochemicals/telomers based on a perfluorohexane (C_6) chain. However, more than 50 enterprises in China that produce AFFF still consume more than 100 tonnes of PFOS per year.

129. As fire-fighting foams have a long shelf life (10–20 years or longer), PFOS-containing fire-fighting foams (FC-600) may still be used around the world in accidental oil fires. In 2004 European Union stocks of fire-fighting foams with PFOS totalled 122 tonnes. In Norway in 2005 the stocks of fire-fighting foams containing PFOS were estimated to be 21 tonnes, with their main use in the off-shore oil industry.[85] In Switzerland stocks of PFOS in 2007 were estimated to be 13 tonnes, with consumption of 15–20% annually.[86] In 2006, Canada reported an estimated 300 tonnes of

[81] http://eippcb.jrc.es/reference/BREF/stm_bref_0806.pdf

[82] Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

[83] The Canadian *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* prohibit PFOS-based fume suppressants in electroless nickel-polytetrafluoroethylene plating and etching of plastic substrates prior to their metalization.

[84] Pabon M, Corpart JM. 2002. Fluorinated surfactants: synthesis, properties, effluent treatment. *Journal of Fluorine Chemistry* 114: 149–156.

[85] Climate and Pollution Agency (former SFT), Norwegian Ministry of the Environment. 2005. Kartleggning av PFOS in brannskum [Survey of PFOS use in fire-fighting foam]. TA-2139.

[86] Buser, A., Morf, L. 2009. Substance flow analysis of PFOS and PFOA in Switzerland. *Environmental Studies* 0922. Federal Office for the Environment, Bern.

stockpiles of PFOS-containing fire-fighting foams, which represents approximately 3 tonnes of PFOS.These stockpiles have partially been destroyed following the coming into force of the *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* in 2008. In Japan stocks of AFFF amount to 19,000 tonnes (50% of which are stored in 23,000 underground parking areas), and the maximum annual production capacity for alternative fire-fighting foams without PFOS is 2,100 tonnes.

130. Collecting and destroying these stocks of PFOS instead of using them will avoid considerable pollution from this persistent organic pollutant (for example, around airports). The cost of replacement and destruction of the PFOS currently found in fire-fighting foam stores in the European Union has been estimated at €6,000 per tonne, or about €700,000 in total. Replacing PFOS throughout Japan with alternatives in an environmentally appropriate way (including collection, refilling, transportation, storage and incineration) would cost ¥1.7 million (€13,000) per tonne, or ¥22 billion (€170 million) in total. In Canada, in 2006, disposal and replacement costs for PFOS-based fire-fighting foams were estimated to be Can$ 700,000 (€500,000).

131. Manufacturers, distributors and users of AFFF fire-fighting agents and their chemical components have formed a not-for-profit trade association, the Fire Fighting Foam Coalition (FFFC), whose stated aim is to ensure that accurate industry information about PFOS alternatives, including telomer-based products, is disseminated to appropriate audiences. The industry position was published in the June 2008 issue of *Asia Pacific Fire Magazine*.[87]

132. The alternatives to the use of PFOS fluorosurfactants in fire-fighting foams are:

(a) Non-PFOS-based fluorosurfactants with shorter chain length such as:

(i) C6-fluorotelomers such as perfluorohexane ethyl sulfonyl betaine, often used in combination with hydrocarbons such as ®Capstone® products (DuPont);

(ii) Dodecafluoro-2-methylpentan-3-one (3M);

(b) A return to the previously used technology, which employed fluorine-free fire-fighting foams. Examples include:

(i) Silicone-based surfactants,[88] often used in combination with fluorosurfactants;

(ii) Hydrocarbon-based surfactants, often used in combination with fluorosurfactants;

(iii) Synthetic detergent foams, often used for forestry and high-expansion applications and for training ("Trainol"); new products with glycols (Hi Combat ATM from AngusFire);[89]

(iv) Protein-based foams (e.g. Sthamex F-15), which are less effective for flammable liquid fuel fires and are mainly used for training but also have some marine uses.

133. FFFC has claimed that fire-fighting foams made from fluorinated surfactants have been shown to be the only technology that can quickly and effectively extinguish fires resulting from highly combustible and flammable materials. Fluorine-free fire-fighting foams can provide an alternative in some applications but cannot provide the same level of fire suppression (capability, durability, etc.).

134. In Norway, the offshore oil industry voluntarily and systematically phased out the use of PFOS before the ban in 2007. PFOS containing fire-fighting foam has also been phased out by other users in Norway. While the most used alternatives in Norway are now PFOS-free telomer-based fluorosurfactants, there are also fluorine-free alternatives on the market, such as Arctic Re-Healing Foam™ RF, developed by 3M Australia. The Norwegian producer Solberg Scandinavian AS states that this fluorine-free alternative is not quite as effective as AFFF and will not be an alternative at offshore installations or for the petroleum industry, but that its fire-fighting performance is close to that of AFFF and that it is a good alternative for other uses. It has been approved for the control and extinguishing of class B flammable liquid hydrocarbon and polar fuel fires. Arctic Re-healing Foam RF meets the requirements of parts 3 and 4 of the European Committee for Standardization (CEN) EN 1568 specifications.[90]

[87] *Asia Pacific Fire Magazine* 26: 2008

[88] Generally, siloxanes such as polyther-modified siloxanes are called silicone surfactants in silicone industry.

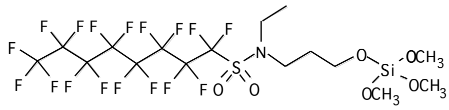
[89] www.kiddecanada.com/utcfs/Templates/Pages/Template-50/0,8061,pageId%3D2587&siteId%3D463,00.html.

[90] Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

135. A British survey states that the fluorine-free alternatives to fire-fighting foams in the United Kingdom are approximately 5–10% more expensive than fluorosurfactant-based foams.[91] According to a manufacturer of fluorine-free alternatives, the price would fall if the market size increased. A more deliberate shift towards fluorine-free fire-fighting foam alternatives would probably eliminate the difference in cost.

N. Other uses

136. According to information from the 2006 OECD survey less than 1 tonne of *N*-ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide (CAS no. 61660-12-6) that is a silane, had been used as an additive in toner and printing inks. Low volumes of PFOS-related substances were also used in sealants and adhesive products.



N-Ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide

O. Summary of the information on alternatives to the use of PFOS

137. The information on alternatives to the use of PFOS is summarized in table 4.

Table 4: Summary of the information on alternatives to the use of PFOS

Use	Use status	Alternatives used
Impregnation of textiles, leather and carpets	PFOS-related substances have been phased out in most OECD countries.	Other fluorinated compounds, like C_6-fluorotelomers and PFBS, silicone-based products, stearamidomethyl pyridine chloride, perfluorobutane sulfonate for leather.[92]
Impregnation of paper and cardboard	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances and phosphates, mechanical processes meaning non-chemical alternatives include extra-dense paper that inhibits leakage of grease through the paper
Cleaning agents, waxes and polishes for cars and floors	PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances, fluorinated polyethers, C_4-perfluorinated compounds. A shift to softer waxes that are more biodegradable or entirely biodegradable may completely eliminate the need for persistent polyfluorinated compounds. In these products, the fluorinated surfactants are replaced with non-ionic or anionic surfactants, which have good wetting properties
Surface coatings, paint and varnish	PFOS-related substances have been phased out in most OECD countries.	Telomer-based compounds, fluorinated polyethers, PFBS, propylated aromatics, silicone surfactants, sulfosuccinates, polypropylene glycol ethers
Oil production and mining	PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.	PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether acids
Photographic industry	A shift to digital techniques has reduced the use drastically.	Telomer-based surfactant products, hydrocarbon surfactants, silicone products,[93] C_3-C_4-fluorinated chemicals. Non-chemical alternatives to PFOS include shifting to digital photography

91 Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

92 Information provided by Argentina in 2011.

93 There are cosiderable datagaps of siloxane compounds used on the market for photographic applications, see reference UNEP/POPS/POPRC.8/INF/17/Rev.1.

Use	Use status	Alternatives used
Electrical and electronic parts	PFOS-based chemicals are or have been used in the manufacture of digital cameras, mobile phones, printers, scanners, satellite communication, radar systems, etc.	For most of these uses, alternatives are considered as available or are being developed.
Semiconductor industry	PFOS is still used but in lower concentrations.	No substitutes with comparable effectiveness have been identified for critical uses, and doing so may take up to 5 years, according to the industry. It should be possible to use PFBS, fluorinated polyethers or telomers for non critical uses only.
Aviation hydraulic oils	PFOS-related compounds may still be used.	Other fluorinated substances and non-fluorinated phosphate compounds could be used.
Pesticides	Sulfluramid is used in Brazilfor control of leaf-cutting ants from the species of *Atta spp.* and *Acromyrmex spp.*. Other fluorosurfactants may be used as inert surfactants in other pesticide products.	Although synthetic piperonyl compounds such as S-Methoprene, Pyriproxyfen, Fipronil and Chlorpyrifos are alternative active substances, sometimes used in combination. Alternative surfactants may exist. Non-chemical alternatives include use of*Metarrhizium anisopliae, Beauveria bassiana and Aspergillus ochraceus.*
Medical devices	Old video endoscopes at hospitals contain a CCD colour filter that contains a small amount of PFOS. PFOS is also used as a dispersant for contrast agents in radio-opaque catheters.	Repairing such video endoscopes requires a CCD colour filter containing PFOS. New CCD filters are PFOS-free. For radio-opaque ethylene tetrafluoroethylene, PFBS can replace PFOS.
Metal plating	PFOS-compounds are still used in hard chrome plating. Cr-III has replaced Cr-VI in decorative chrome plating.	Some non-fluorinated alternatives are marketed but they are not considered equally effective in hard chrome plating. A C_6-fluortelomer is used as a substitute and may be effective. PFBS derivatives may also be used. Non-chemical alternatives include physical barriers that may also be used
Fire-fighting foams	The use of PFOS-related substances in new products has been phased out in most OECD countries. Stocks are still being used up.	C_6– fluorotelomers are used as substitutes in new products; fluorine-free alternatives are used for training exercises and possibly in other settings than offshore.

IV. Properties of alternative substances and hazard assessment

A. Overview

138. This chapter contains a brief description of the environmental, safety and health properties of PFOS alternatives. For some of these alternatives, a general discussion of properties might be all that is possible owing to a lack of specific information. For each of the chemical groups discussed, a more comprehensive compilation of information was beyond the scope of the present study. More detailed information on the properties of the alternatives is provided in the Technical paper on the identification and assessment of alternatives to PFOS in open applications.[94]

139. The key to the performance of fluorosurfactants is extremely low surface tension. Currently, no other surfactant can match the low surface tension of PFOS. Because of environmental and health concerns and the often high prices of fluorosurfactants, however, other surfactants should be used as alternatives where very low surface tension levels are not needed.

140. When production of PFOS ceased in the United States in 2002, other chemicals took their place in the US, but PFOS production rapidly increased in China.[95] They were mainly derivatives of perfluoroalkyl sulfonates with a shorter alkyl chain and C_8-based fluorotelomers. Since 2006, the major manufacturers of C_8-based telomers (8:2 fluorotelomers) in the EU, Japan, and US have been working towards the elimination of C_8-based and longer-chain-based PFCs by 2015, in accordance with the

[94] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[95] UNEP-POPS-POPRC-SUB-F08-PFOS-ADIN-CHI.English.pdf

United States Environmental Protection Agency's voluntary 2010/2015 PFOA Stewardship Program.[96] Producers outside these regions are not included in the partnership. Currently, C_6-fluorotelomers increasingly dominate the trade. Thus far it has been difficult for non-fluorinated alternatives to gain a firm foothold in the market, partly because of established supplier relationships and partly due to regulatory policies that permit continued use of fluorinated chemicals in commerce.

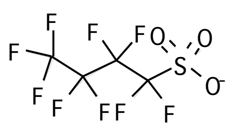
141. Table 5 gives a brief overview of groups of chemical alternatives to PFOS.

Table 5: Overview of main chemical alternatives to PFOS compounds

Alternative compound	Product trade name	Company	Uses
Perfluorobutane sulfonate (PFBS) derivatives or other alternatives based on various C_4-perfluorocompounds	Novec® Scotchgard®	3M	Paint and coatings industry, electronic coatings, industrial and commercial cleaning, stain protectors for carpets and leather, furniture, automotive uses, hard surfaces and other apparels, catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression, rubber moulding defoamers in electroplating, etc.
Perfluorobutyl methyl ethers	Novec®	3M	Industrial cleaning
Dodecafluoro-2-methylpentan-3-one	Novec® 1230	3M	Fire-fighting foams
Polyfluorodialkyl ether sulfonates	F-53, F-53B	Shanghai SYNICA[97]	Mist suppressant hard chrome plating
Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	3M	Hydraulic fluids
Fluorotelomer alcohol (FTOH) based chemicals and polymers	Capstone®	DuPont	Surfactants, coatings, printing, textile and chemical industries, chrome plating
C_6 fluorotelomer sulfonamide compounds	Forafac™ 1157, 1183, 1157N and 1203	DuPont	Fire-fighting foams
Fluorinated co-polymers	Foraperle® 225, etc.	DuPont	Impregnation of leather and indoor car upholstery
CF_3 or C_2F_5 fluoroalkyl polyethers	PolyFox®	OMNOVA Solutions Inc.	Surfactant and wetting additives for coating formulations and floor polish
Propylated naphthalenes or biphenyls	Ruetasolv®	Rütgers Kureha Solvents	Water-repelling agents for rust protection systems, marine paints, coatings, etc.
Sulfosuccinate	Lutensit®	BASF	Levelling and wetting agents
	Edaplan® LA 451	Münzing Chemie	Paint and coating industry: wetting and dispersing agents for water-based applications such as wood primers
	Hydropalat®875	Cognis	
Siloxanes and silicone polymers	WorléeAdd®	Worlée-Chemie	Wetting agents in the paint and ink industry
	Advantex®	Bluestar Silicones	Impregnation of all-weather textiles. Also related products for car polish, cleaners, anti-foaming agents, car waxes
Polypropylene glycol ethers	Emulphor® Enthone	BASF Cookson Electronics	Levelling and wetting agents Decorative chrome plating, etc.

B. Shorter-chain perfluoroalkyl sulfonates

142. After the phase-out of PFOS, 3M introduced a new generation of polymeric anionic fluorinated surfactants (Scotchgard® and Novec® products), which are based on perfluorobutane sulfonates (PFBS; C_4-chemistry):



96 www.epa.gov/oppt/pfoa/pubs/stewardship/index.html

97 www.synica.com.cn/zk/cn/products.asp?id=5&id2=72

143. These compounds are claimed to have a low dynamic surface tension or rather a rapid surface migration, which is important in high-speed coating processes and low-viscosity systems. Generally these surfactants have a lower surface tension than hydrocarbon and silicone surfactants. They can also be used in smaller amounts than hydrocarbon surfactants. The compounds are said to influence the adhesion of the second-layer coating less than silicon or conventional fluorinated surfactants.

144. These short-chain alternatives could provide the surfactant function in various applications including the paint and coatings industry; stain-repellent impregnation of textiles, leather and carpets; in electronic coating; in industrial commercial cleaning; and in cleaners for solder flux residue.

145. According to information from the 2006 OECD survey, 50–160 tonnes of potassium perfluorobutane sulfonate and 40–60 tonnes of perfluorobutane sulfonyl fluoride were produced in 2005 as intermediates for the production of catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression systems, rubber molding defoamers for electroplating and the like.

1. Health effects of shorter-chain perfluoroalkyl sulfonates

146. Information about PFBS, its potassium salt (PFBSK) and PFHxS (C6) is available. Extensive toxicity studies are not available. However a variety of impacts of C6-C4 substances have been observed in peer-reviewed studies including attention deficit hyperactivity disorder in children, negative impacts on development in animals, and modulation of immune system response. The substances have also been detected in cord blood, adult blood, house dust, sea mammals and in the Arctic.[98]

147. It has been claimed that PFBS does not have the particularly serious toxic effects associated with PFOS and other long-chain analogues. A number of peer reviewed studies have examined the potential toxicity and indications of human toxicity, immunotoxic properties in vitro, genotoxicity and neurotoxicity of PFBS along with other PFCs.[99] Since extensive toxicity data exist, published in peer-reviewed literature, the toxicity concerning PFBS to some extent known to science. However there are still data gaps.[100, 101]

148. PBFS and PFHxS among other PFCs have been found in blood and serum of humans, PFBS being the predominant PFC found in humans.[102] Elevated levels in humans of PFOS, PFOA, and PFNA beside PFHxS have been found in several peer reviewed studies.[103] PFHxS is associated with elevated odds of high cholesterol in humans and deficit/hyperactivity disorder in children 12-15 years old. Increasing umbilical cord concentrations of PFHxS were associated with decreasing birth weight and decreasing birth length in humans.[104]

2. Environmental effects of shorter-chain perfluoroalkyl sulfonates

PFBS is a strongly acidic and highly water-soluble and persistent substance which has a low vapour pressure and is poorly adsorbed to soils and sediments, and is therefore expected to remain in the water compartment on release into the environment. PFBS stays mostly in the water column as its water solubility is much higher than that of higher homologues. PFBS has been widely detected in water and has very low sorption. PFBS is also found in municipal landfill leachates, drinking water and in the Arctic. PFBS has been found in indoor dust from homes and offices.[105] According to the information provided by Germany in 2011 and peer reviewed publications, due to the very limited ability of the <C6-bodies to adsorb, it is difficult to remove the chemicals from water.[106] Until now, no method is known. In water samples from rivers and certain groundwater, the short-chain PFCs can already be detected. PFHxS and other PFCs are found in polar bears and humans in the Arctic.[107, 108]

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98 See appendix A.

99 See appendix A.

100 UNEP/POPS/POPRC.8/INF/17/Rev.1

101 Posner et.al, "Per- and polyfluorinated substances in the Nordic Countries, Use, occurence and toxicology", TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013).

102 See appendix A.

103 See appendix A.

104 Lee Yj, Kim MK, Bae J, Yang JH (2013) Concentrations of perfluoroalkyl compounds in maternal and umbilical cord sera and birth outcomes in Korea, Chemosphere 90:1603-1609.

105 See appendix A.

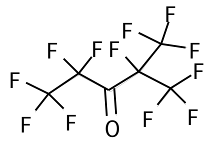
106 See appendix A.

107 Hanssen L, Dudarev AA, Huber S, Odland JO, Nieboer E, Sandanger TM (2013) Partition of perfluoroalkyl substances (PFASs) in whole blood and plasma, assessed in maternal and umbilical cord samples from inhabitants of arctic Russia and Uzbekistan, Sc Total Environ doi: 10.1016/j.scitotenv.2013.01.029.

Increasing levels of PFHxS have been found in samples from Beluga whales from Alaska between 1989 and 2006.[109]

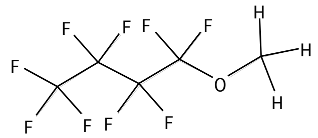
C. Shorter-chain perfluoroalkyl ketones and ethers

149. According to 3M's website, a C_6-fluorinated compound, Novec™ 1230, is used as a gaseous fire suppression agent produced by that company. The compound is dodecafluoro-2-methylpentan-3-one (CAS no. 756-13-8):



Dodecafluoro-2-methylpentan-3-one

150. 3M also markets some C_4-perfluorinated compounds for commercial and industrial cleaning under the trademark Novec™, such as methyl nonafluorobutyl ether (CAS no. 163702-07-6) and methyl nonafluoroisobutyl ether (CAS no. 163702-08-7). Here the methyl group is not fluorinated.



Methyl nonafluorobutyl ether

1. Health effects of shorter-chain perfluoroalkyl ketones and ethers

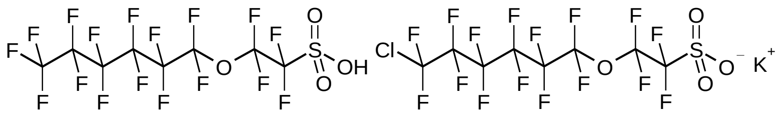
151. No data are available.

2. Environmental effects of shorter-chain perfluoroalkyl ketones and ethers

152. Published peer-reviewed data are lacking.

D. Polyfluorodialkyl ether sulfonates

153. In China F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate) and F-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) are available as PFOS alternatives for chrome plating.[110] The structure formulas of F-53 and F-53B are, respectively:



1. Health effects of polyfluorodialkyl ether sulfonates

154. No data are available.

2. Environmental effects of polyfluorodialkyl ether sulfonates

155. No data exist other than Epi Suite model results for persistence (half-lives) in water, sediment, soil and air, bioconcentration factors (BCFs).[111]

[108] Bytingsvik J, van Leeuwen SP, Hamers T, Swart K, Aars J, Lie E, Nilsen EM, Siig O, Derocher AE, Jenssen BM (2012) Perfluoroalkyl substances in polar bear mother-cub pairs: a comparative study based on plasma levels from 1998 and 2008, Environ Int 49:92-99

[109] Reiner JL, O'Connel SG, Moors AJ, Jucklick JR, Becker PR, Keller JM (2011) Spatial and temporal trends of perfluorinated compounds in Beluga whales (Delphinapterus leucas) from Alaska, Environ Sci Technol 45:8129-8136

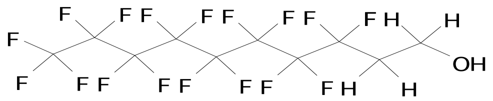
[110] Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

[111] UNEP/POPS/POPRC.8/INF/17/Rev.1.

E. Fluorotelomers and fluorophosphates

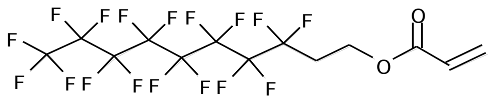
156. In general, both long and short chain fluorotelomers have been the most common alternatives to PFOS compounds.[112] They are not fully fluorinated but contain more reactive hydrocarbon parts and functional groups. The perfluorinated tail, however, is similar to the tail of PFOS and is as persistent, and these chemicals are precursors of perfluorinated carboxylic acids (PFCAs). According to information from the 2006 OECD survey, more than 5,000 tonnes of PFCA precursors were produced and used in 2005.

157. One of the basic structures is 8:2 fluorotelomer alcohol (8:2 FTOH), also named 1*H*,1*H*,2*H*,2*H*-perfluorodecanol; it has a C_8-perfluorinated tail:



158. DuPont specializes in fluorotelomers and markets a wide range of Zonyl® products, generally associated with 8-2 alcohol-based products, and Capstone® products, generally associated with 6:2-fluorotelomer-based products.

159. An acrylate of fluorotelomer with the name of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (CAS no. 27905-45-9) has been marketed by DuPont as a telomer intermediate under the trade name of Zonyl® TA-N:



160. As was mentioned, these two chemicals are covered by the U.S. EPA's 2010/15 PFOA Stewardship Program for voluntary phase-out by companies in Japan, EU, and US.While the shorter- and longer-chain telomers are not subject to the voluntary agreement, they are covered in the US by the recent United States Environmental Protection Agency action plan for long-chain PFCs.[113]

161. DuPont manufactures a range of fluorotelomers called DuPont® Forafac® products, with 65–95% C_6-fluorinated amphoteric telomers based on perfluorohexyl ethyl sulfonamide, which are used in fire-fighting foam formulations.[114] A possible structure formula for an amphoteric compound 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctane sulfonamidopropyl carboxybetaine, which now replaces the analogous fully fluorinated perfluorooctane compound, is:

[112] Long-chain" has been defined by the Organisation for Economic Cooperation and Development (OECD) for two classes of perfluoroalkyl substances: perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs). The definition is posted on the OECD Portal on Perfluorinated Chemicals at http://www.oecd.org/ehs/pfc/

Text from the website: "A distinction is made between long-chain perfluorinated compounds (LC PFCs) and short-chain perfluorinated compounds (SC PFCs), based on the toxicity and bioaccumulation differences between LC PFCs and SC PFCs." Long-chain perfluorinated compounds" refers to:

(a) Perfluorocarboxylic acids with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA);

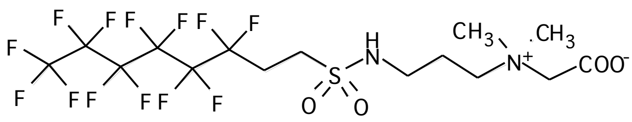
(b) Perfluoroalkyl sulfonates with carbon chain lengths C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS); and

(c) Precursors of these substances that may be produced or present in products.

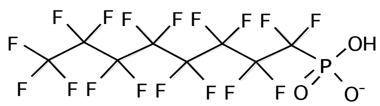
(d) For definition purposes "precursor" means a substance that has been recognized as having the potential to degrade to perfluorocarboxylic acids with a carbon chain length of C8 and higher (including PFOA) or perfluoroalkyl sulfonates with a carbon chain length of C6 of higher (including PFHxS and PFOS)."Short-chain therefore is defined as perfluorocarboxylic acids with carbon chain lengths C7 and shorter and perfluoroalkyl sulfonates with carbon lengths C5 and shorter as well as potential precursors to these substances.

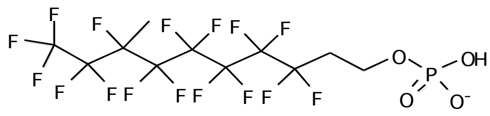
[113] www.epa.gov/oppt/existingchemicals/pubs/pfcs_action_plan1230_09.pdf

[114] www2.dupont.com/Forafac/en_US/index.html

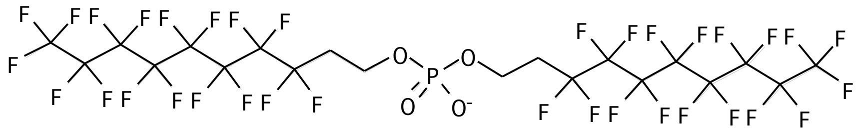


162. The polyfluoroalkyl phosphonic acids and phosphoric acids and their diesters (PAPs and diPAPs), used mainly in food packaging, have recently been discovered in the environment and in people.[115] Here are examples of structure formulas:





Perfluorooctyl phosphonate 8:2 PAP



8:2 diPAP

163. DuPont markets more Zonyl products in this group, such as Zonyl® 9027, a spot and dirt repellent, which is a telomer B phosphate diethanolamine (CAS no. 65530-63-4). Again, these chemicals are based on C_8-fluorine chemistry and are to be voluntarily phased out in Japan, EU, and USby December 31, 2015.[116] Similar chemicals with shorter chain lengths may still be used.

164. The C_8-telomer-based materials are disappearing in favour of C_6-based materials. C_6-based materials are inherently more expensive (by a substantial amount) than C_8- or telomer-based materials.[117]

1. Health effects of fluorotelomers and fluorophosphates

165. There is a lack of health data for the many specific and complex fluorotelomers used in practice. Some of their degradation products are known to have adverse health impacts. For example, PFOA is found in breast milk and has been shown to be tumorigenic and immunotoxic in laboratory animals. Higher concentrations of serum PFOA are associated with osteoarthritis in women.[118] In humans, in utero exposure to PFOA is associated with lower sperm concentration, lower total sperm count, higher levels of lutenizing hormone, and higher levels of follicle stimulating hormone.[119] A study of placental transfer found a strong correlation between PFOA concentrations in pregnant women and the cord blood of their respective newborns.[120] Japanese researchers have shown that PFOA can alter the expression of over 500 genes,[121] while Chinese researchers investigating the genotoxic potential of PFOA in human liver cells (hepatoma HepG2 cells) in culture have

[115] D'eon JC, Crozier PW, Furdui VI, Reiner EJ, Libelo EL, Mabury SA. 2009. Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers. *Environmental Science and Technology* 43: 4589–4594.

[116] http://www.epa.gov/oppt/pfoa/pubs/stewardship/

[117] Personal communication from Richard Thomas, affliation here, January 2010.

[118] Uhl SA, James-Todd T, Bell ML (2013) Association of osteroarthritis with perfluorooctanoate and perfluorooctane sulfonate in NHANES 2003-2008.

[119] Vested A, Ramlau-Hansen CH, Olsen SF, Bonde JP, Kristensen SL, Halldorsson TI, Becher G, Haug LS, Ernst EH, Toft G (2013) Associations of in utero exposure to perfluorinated alkyl acids with human semen quality and reproductive hormones in adult men, Environ Health Perspect, DOI:10.1289/ehp.1205118.

[120] Porpora MG, Lucchini R, Abballe A, Ingelido AM, Valentini S, Fuggetta E, Cardi V, Ticino A, Marra V, Fulgenzi AR, Felip ED (2013) Placental transfer of persistent organic pollutants: a preliminary study on mother-newborn pairs, Int J Environ Res Public Health 10:699-711.

[121] Guruge KS, Yeung LW, Yamanaka N, Miyazaki S, Lam PK, Giesy JP, Jones PD, Yamashita N., Gene Expression Profiles in Rat Liver Treated With Perfluorooctanoic Acid (PFOA). *Toxicol Sci*. 2005 Oct 12; [Epub ahead of print].

demonstrated that PFOA exerts genotoxic effects on these cells, probably through oxidative DNA damage.[122] Increasing toxicological or ecotoxicological information are becoming available for the degradation produts other than PFOA. In vitro studies demonstrate impaired reproduction and altered sex hormone levels.[123, 124] They have been regularly detected in human blood, umbilical cord blood and breast milk and the data that exists suggest similar characteristics as previously observed with PFOA. They are also found in consumer products, offices, food packaging and food.[125,126,127,128,129,130]

2. Environmental effects of fluorotelomers and fluorophosphates

166. There is also a lack of environmental data on the fluorotelemers and fluorophosphates used in practice. Some are volatile and may undergo long-range air transportation. They degrade to perfluorinated carboxylic acids, such as perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA), in organisms and in nature. These perfluorinated acids have been widely detected in the environment and wildlife.[131] PFOA has been found in the Arctic environment, and reaches very high levels (for example in sea-ice snow pack in the Arctic, PFOA is detected at levels that are higher than already banned POPs, such as PCBs and POP-BDEs).[132]

167. The environmental hazard, including tendency to bioaccumulation, increases with chain length, and all perfluorinated alkyl chains are completely persistent in nature.

F. Fluorinated co-polymers

168. DuPont markets many Zonyl® co-polymers for various purposes, such as Zonyl® G Fabric Protector for textiles, which consists of 2-methyl-2-propenoic acid dodecyl ester polymer with 10-15% α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl poly(difluoromethylene) (CAS no. 65605-58-5).

169. Foraperle® 225 (DuPont) is an acrylic fluorinated co-polymer (25%) in a solvent medium (75% butyl acetate) used for finishing and protection of leathers and car upholstery through water and oil repellence. It contains the compound 2-propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate, γ-ω-perfluoro-C_{10}-C_{16}-alkyl acrylate and stearyl methacrylate (CAS no. 203743-03-7). Another acrylic fluorinated co-polymer is dodecyl methacrylate polymer with α-fluoro-ω-[2-[(1-oxooctadecyl)oxy]ethyl]-poly(difluoromethylene) (CAS no. 65530-65-6), which is used in a concentration of 0.085–0.45%.

170. The substance 2-propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate, γ-ω--perfluoro-C_{10}-C_{16}-alkyl acrylate and stearyl methacrylate (CAS no. 203743-03-7) has been prohibited in Canada under the *Prohibition of Certain*

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122 Yao X. & Zhong L., Genotoxic risk and oxidative DNA damage in HepG2 cells exposed to perfluorooctanoic acid. *MutationResearch/Genetic Toxicology and Environmental Mutagenesis* Volume 587, Issues 1-2 , 10 November 2005, Pages 38-44.

123 Liu C, Deng J, Yu L, Ramesh M, Zhou B (2010) Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alchohol, Aquat Toxicol 96:70-76.

124 Liu C, Yu L, Deng J, Lam PK, Wu RS, Zhou B (2009) Waterborne exposure to fluorotelomer alcohol 6:2 FTOH alters plasma sex hormone and gene transcription in the hypothalamic-pituitary-gonadal (HPG) axis of zebrafish, Aquat Toxicol 93:131-137.

125 Herzke D, Olsson E, Posner S (2012) Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study, Chemosphere 88:980-987.

126 Fraser AJ, Webster TF, Watkins DJ, Nelson JW, Stapleton HM, Calafat AM, Kato K, Shoeib M, Vieira VM, McClean MD (2012) Polyfluorinated compounds in serum linked to indoor air in office environments, Environ Sci Technol 46:1209-1215.

127 Gebbink WA, Ullah S, Sandblom O, Berger U (2013) Polyfluoroalkyl phosphate esters and perfluoroalkyl carboxylic acids in target food samples and packaging-method development and screening, Environ Sci Pollut Res Int .

128 De Silva AO, Allard CN, Spencer C, Webster GM, Shoeib M (2012) Phosphorus-containing fluorinated organics: polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluorophosphonates (PFPAs), and perfluorophosphinates (PFPIAs) in residential indoor dust, Environ Sci Technol 46:12575-12582.

129 Liu W, Takahashi S, Sakuramachi Y, Harada KH, Koizumi A (2013) Polyfluorinated telomers in indoor air of Japanese houses, Chemosphere 90:1672-1677.

130 Xu Z, Fiedler S, Pfister G, Henkelmann B, Mosch C, Volkel W, Fromme H, Schramm KW (2013) Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany, Sci Total Environ 443:485-490.

131 See appendix A.

132 Information provided by Inuit Circumpolar Council in 2011.

Toxic Substances Regulations, 2012 as it is a precursor to long-chain PFCAs. The following substances are also prohibited:

(a) Hexane,1,6-diisocyanato-, homopolymer, reaction products with α-fluoro-ω-2-hydroxyethyl-poly(difluoromethylene), C16-20-branched alcohols and 1-octadecanol;

(b) 2-propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with butyl 2-propenoate and 2,5-furandione, γ-ω-perfluoro-C8-14-alkyl esters, tert-Butyl benzenecarboperoxoate-initiated;

(c) 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylene tetramine.

171. In most instances the exact composition of the products and their active substances have not been disclosed by the private sector.

1. Health effects of fluorinated co-polymers

172. There is a lack of specific health data on the active fluorinated substance. Polymers are generally of low availability/uptake and have low toxicity but there is a lack of data to confirm this relation for fluorinated polymers.[133]

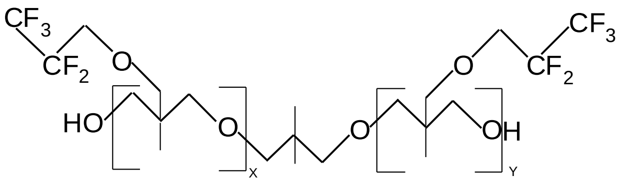
2. Environmental effects of fluorinated co-polymers

173. There is a lack of data. The ultimate degradation products may be perfluoroalkanoic acids (PFAAs), including PFOA.

G. Fluorinated polyethers

174. OMNOVA Solutions Inc. produces under the trade name PolyFox™ a family of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C_2F_5 or CF_3 perfluoroalkyl side chain structures. The PolyFox™ product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols.

175. The basic structure of PolyFox™ 656 compounds is illustrated in the following figures (x + y equals about 6):



176. It seems that these surfactants have a moderate surface tension that is not quite as low as that of conventional fluorinated surfactants. The new surfactants are claimed to have a broad processing window, with less interference with other compounds. Coating quality is improved as foaming is reduced. The latter is an important factor in producing and processing water-borne coatings.

177. PolyFox™ fluorosurfactants have been used in aqueous and solvent-borne semiconductor coating formulations. In a number of examples excellent wetting, flow and levelling properties have been achieved for semiconductor coatings.

178. In addition, the poly(alkylene oxide) chain of all PolyFox® materials has an inherently low refractive index compared to other commercial polymers such as acrylics. The presence of even very short ($-CF_3$, $-C_2F_5$) side chains further reduces the refractive index, and PolyFox® materials have been used as antireflection layers in photo-resist and LCD screen applications. The PolyFox® formulation is currently being used as a surfactant in floor polish products in the United States, Europe and Asia.

179. PolyFox® products are currently priced competitively in comparison with any new C_6-based materials but are more expensive than the C_8-based materials, which is being phased out.[134]

1. Health effects of fluorinated polyethers

180. The acute toxicity of fluorinated polyethers is low (LD_{50}> 2 g/kg bw) but they may irritate skin and the respiratory system. Generally, data are lacking.

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[133] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[134] Personal communication from Richard Thomas, OMNOVA, January 2010.

2. Environmental effects of fluorinated polyethers

181. The polymer backbone linkage of the PolyFox® molecules is an ether link, which is more environmentally stable than, for example, the ester/amide links of PFOS and telomer-based fluorosurfactants. This makes the PolyFox® molecule more persistent and resistant to degradation to lower molecular weight carboxylic acids.

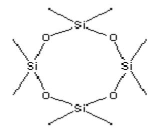
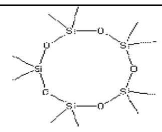
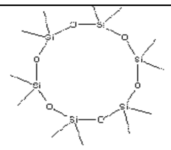
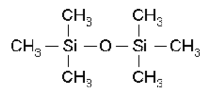
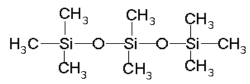
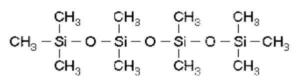
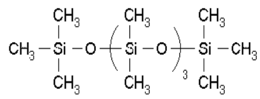
H. Siloxanes and silicone polymers

182. Silicones are mainly polymers with the generic formula R_2SiO.[135] They may be straight-chain or cyclic compounds and vary in molecular weight from a few hundred to several hundred thousand g/mol for the polymers The building blocks of silicones are either siloxanes or silanes. Siloxanes are organic group substituted silica with the chemical formula $[R_2SiO]_n$, where R is an organic substituent such as methyl, ethyl, phenyl, etc. The chemicals formula for silanes is $(R)_n$-$1SiX_n$, where n=0-4, X=Halogen (usually chlorine), R= organic substituent (usually CH3).

183. Commercial products of polysiloxanes, that are alternatives to PFOS, may contain principal siloxanes of concern from an environmental and health perspective. These siloxanes are volatile methyl siloxanes with short SiO backbones, in particular the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes MM (or HMDSO), MDM, MD2M and MD3M. They are shown in table 6.

[135] http://www.dowcorning.com/content/publishedlit/51-960A-01.pdf

Table 6: Siloxanes of environmental and health concern, that may appear as impurities in commercial polysiloxanes[136]

Abbreviation	Name	CAS no.	Structure
D4	Octamethyl cyclotetrasiloxane	556-67-2	
D5	Decamethyl cyclopentasiloxane	541-02-6	
D6	Dodecamethyl cyclohexasiloxane	540-97-6	
MM (or HMDSO)	Hexamethyl disiloxane	107-46-0	
MDM	Octamethyl trisiloxane	107-51-7	
MD2M	Decamethyl tetrasiloxane	141-62-8	
MD3M	Dodecamethyl pentasiloxane	141-63-9	

184. Out of these commercially used siloxanes, D4, D5, and MM (or HMDSO) are chemicals produced in high volumes in the European Union. The first two are the most commonly used siloxanes in the Nordic countries.[137]

185. Recent activities in the northern hemisphere have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as sealants, fuels, car polishes, cleaners, anti-foaming agents, car waxes and personal care and biomedical products.[138] The widespread use of siloxanes and their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they are widespread in the environment.

186. Silicone polyethers are another class of silicone derivatives that have special surfactant properties. The leading manufacturers are Bluestar, Dow Corning, Evonik-Goldschmidt, Momentive and Wacker. Other companies sell specially formulated mixtures for specific applications.

187. Bluestar Silicones markets some PFOS alternatives based on silicone for textile applications under the trade name Advantex®.

188. Worlée-Chemie produces silicone polymers, which in the paint and ink industry can in several cases be used as alternatives to fluorosurfactants as wetting agents. WorléeAdd® 340 is a low-viscous non-ionic special modified silicone polyether (containing 3-(polyoxyethylene) propylheptamethyl trisiloxane, CAS no. 67674-67-3) that can improve surface wetting of aqueous systems on difficult substrates like polyethylene and polypropylene or contaminated substrates. It has a low surface tension and is claimed to be highly effective in improving wetting, spreading and levelling of water-borne

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[136] Cousins AP, Kaj L, Broström-Lundén E. 2009. Siloxanes in the Nordic environment. *Norman Bulletin* no. 1. www.norman-network.net.

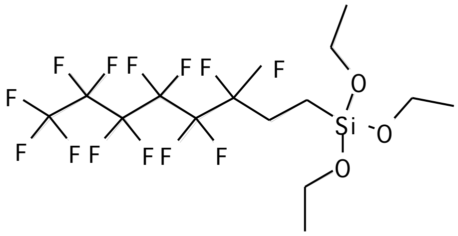
[137] Kaj L, Schlabach M, Andersson J, Cousins AP, Schmidbauer N, Brorström-Lundén E. 2005. Siloxanes in the Nordic Environment. TemaNord 2005:593.

[138] Lassen C, Hansen CL, Mikkelsen SH, Maag J. 2005. Siloxanes – consumption, toxicity and alternatives. Environmental Project no. 1031. Danish Environmental Protection Agency.

coatings and eliminating surface defects without foam stabilizing. It is further claimed that the compound normally has no negative effect on recoating.

189. Another product, WorléeAdd® 345, is a mixture of a silicone polyether (10–15%) and a dioctyl sulfosuccinate (50–55%) in ethanol and water. This surfactant can be used to improve wetting properties of aqueous coatings for different substrates, where penetration into absorbing surfaces also is improved.

190. Perfluoroalkyl derivatives of silanes also exist; they include 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl triethoxysilane, which is effective for glass and surface trea®ent.[139] One compound, polyfluorooctyl triethoxysilane (1*H*,1*H*,2*H*,2*H*-perfluorooctyl triethoxysilane), has been banned in Denmark. The formula is:



1. Health effects of siloxanes and silicone polymers

191. 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, which is 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/m^3 was derived, based on lung toxicity, including a safety factor of 250.[140] Some years ago polysiloxanes or silicone polymers were evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC).[141] Low-molecular-weight polydimethylsiloxanes have been studied by siloxane manufacturers and they conclude that the polydimethylsiloxanes studied all possess a very low potential for toxicity.

192. The Scientific Committee on Consumer Products in the European Union has published an Opinion on D4 in which the safety of D4’s use as a cosmetic ingredient has not been questioned.[142] In the United States, the Cosmetic Ingredient Review (CIR) panel is about to publish its final assessment of the safety of cyclic siloxanes, D3, D4, D5, D6 and D7.[143] The panel has concluded that D4, D5, D6 and D7 are safe for use in cosmetics. D3 will be taken off the International Nomenclature of Cosmetic Ingredients (INCI) list because it is not a commercial product.

193. Other studies of siloxanes, however, indicate that they seem to be harmful when inhaled and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact with WorléeAdd® 340 may cause skin irritation.[144] In short, knowledge of the toxicity of siloxanes is still incomplete.

194. The polyfluoroalkyl siloxane was banned in Denmark because of lung damage in experimental mice.[145]

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[139] ABCR 2006–2007 catalogue: Fluorochemicals. Karlsruhe, Germany.

[140] Greve K, Nielsen E, Ladefoged O. 2008. Toxic effects of siloxanes: group evaluation of D3, D4, D5, D6 and HMDS in order to set a health-based quality criterion in ambient air. *Toxicology Letters* 180: S67.

[141] http://www.ecetoc.org/index.php?mact=MCSoap,cntnt01,details,0&cntnt01by_category=3&cntnt01order_by=Reference%20Desc&cntnt01template=display_list_v2&cntnt01display_template=display_details_v2&cntnt01document_id=5338&cntnt01returnid=91

[142] http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_029.pdf

[143] http://ijt.sagepub.com/content/30/6_suppl/149S.abstract

[144] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[145] Nørgaard AW, LarsenST, Hammer M, Poulsen SS, Jensen KA, Nielsen GD, Wolkoff P. 2010. Lung damage in mice after inhalation of nanofilm spray products: the role of perfluorination and free hydroxyl groups. *Toxicological Sciences* 116 (1): 216–224.

2. Environmental effects of siloxanes and silicone polymers

195. Siloxanes are widely distributed in the northern hemisphere. In general, siloxanes are very stable and persistent compounds that do not degrade in the environment. They are also found in the Arctic. However, there are some studies which conclude that siloxanes are unlikely to meet the POP screening criteria for long range transport,[146, 147] The cyclic- and short-chain linear siloxanes bioconcentrate in aquatic organisms.[148] These siloxanes may be toxic to aquatic organisms and are bioaccumulative; there are, however, still gaps in our knowledge.

196. According to the material safety datasheet for WorléeAdd® 340, the silicone polymer in that product is classified as environmentally dangerous with the R-phrases R51 (“Toxic to aquatic organisms”) and R53 (“May cause long-term adverse effects in the aquatic environment”). The R-phrase R53 indicates that the substance is bioaccumulative.

197. The cyclic siloxanes D4, D5 and D6 have been subjected to an environmental risk assessment by the United Kingdom Environment Agency applying European Union Technical Guidance.[149] Canada has concluded that D4 has the potential to cause harm in the aquatic environment and has implemented a risk management measure to reduce release from industrial effluents. Environment Canada has additionally concluded that D5 has no risk environmentally (no PbiT) based upon the recommendation done by the BOR. Also, D6 has been ommited from their assessment list.[150]

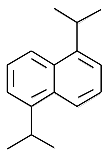
198. A review of the environmental properties of cyclic siloxanes is available on the Internet.[151] In-depth information on the properties of siloxanes is provided in the Technical paper on the identification and assessment of alternatives to PFOS in open applications.[152]

I. Propylated aromatics

199. Rütgers Kureha Solvents produces various aromatic surfactants with the trade name Ruetasolv®; based on propylated naphthalenes and biphenyls, these products can be used as water-repelling agents for different applications such as corrosion protection systems, marine paints, resins, printing inks, coatings and electrical, electronic and mechanical applications.

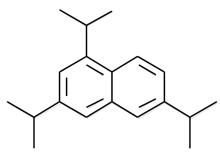
200. They may also be used as plasticizers and film-forming aids in emulsion paints and adhesives. The various isopropyl naphthalenes and isopropyl biphenyls are very hydrophobic substances that are compatible with almost all raw materials such as epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate co-polymers, mineral oils and bitumen.

201. Propylated aromatic products are all colourless liquids with a boiling point of about 300°C and have very low solubility in water.



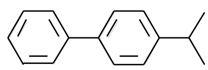
Ruetasolv DI

CAS no. 38640-62-9



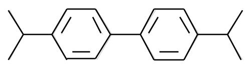
Ruetasolv TTPN

CAS no. 35860-37-8



Ruetasolv BP 4201

CAS no. 69009-90-1



Ruetasolv BP 4103

CAS no. 25640-78-2

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146 http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQZ-e-e.pdf
D5 http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQX-e-e.pdf
D6 http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQY-e-e.pdf

147 http://www.sciencedirect.com/science/article/pii/S0045653512012842
http://www.sciencedirect.com/science/article/pii/S0045653512012957
http://www.sciencedirect.com/science/article/pii/S0045653512012933

148 Parrott JL, Alaee M, Wang D, Sverko E (2012) Fathead minnow (Pimephales promelas) embryo to adult exposure to decamethylcyclopentasiloxane (D5), Chemosphere doi: 10.1016/j.chemosphere.2012.10.053.

149 http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/batch-lot-2/index-eng.php

150 http://www.cdr-siloxaned5-bor.ca/default.asp?lang=En&n=70551E34-1

151 www.cyclosiloxanes.eu

152 UNEP/POPS/POPRC.8/INF/17/Rev.1.

1. Health effects of propylated aromatics

202. The substances *p*-isopropyl-1,1'-biphenyl (Ruetasolv BP 4103) and *p,p*'-diisopropyl-1,1'-biphenyl (Ruetasolv BP 4201) can cause skin sensitization or dermatitis upon repeated contact with skin, and long-term exposure causes irritation of the eyes, nose, throat, mucous membranes and respiratory tract. *p*-Isopropyl-1,1'-biphenyl has a very low acute toxicity with oral LD_{50} values for rats of > 4 g/kg. Central nervous system, liver and kidney damage have, however, been reported as chronic effects of that chemical in animals.[153]

203. Isopropylated naphthalenes are also irritating substances. The acute toxicity of diisopropylnaphthalene (Ruetasolv DI) is very low, with an oral LD_{50} value for rats of 3,900 mg/kg.[154]

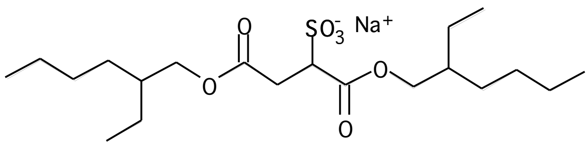
2. Environmental effects of propylated aromatics

204. The biphenyls and the naphthalenes have high octanol/water partition coefficients (log K_{OW}), and the bioconcentration factor (BCF) for the substances is greater than 100. These chemicals are therefore potentially bioaccumulative. The biphenyl moiety seems to be easily biodegradable, whereas the naphthalene moiety biodegrades slowly. The sparse available information suggests that the biphenyls are acutely toxic to aquatic organisms, whereas naphthalene appears to have no acute toxic effects on the investigated fish species.[155]

J. Sulfosuccinates

205. Several companies produce surfactants based on 50–75% of the sodium salt of di(2-ethylhexyl) sulfosuccinate, which can be used as a wetting agent for aqueous systems of detergents, cleaners, paints and coatings. It is also used in pesticides.

206. In the following, the chemical structure of the sodium salt of di(2-ethylhexyl) sulfosuccinate (CAS no. 577-11-7) is presented:



207. In a product from BASF (Lutensit® A-BO) the sulfosuccinate is mixed with water and ethanol, and in a product from Cognis (Hydropalat® 875) the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol.

208. The product from Cognis can be used as a wetting agent in aqueous coating systems and is particularly suitable for difficult-to-wet substrates like plastics, metal, cellulose film, silicone-treated papers and glass. This surfactant may also be used as an emulsifier for emulsion polymerization. Another area where it can be used as an alternative to fluorinated surfactants is in optimizing the colour acceptance of aqueous pigment concentrates in different coatings. The product has medium foam formation.

209. Münzing Chemie also produces a surfactant (Edaplan® LA 451) based on a sulfosuccinate derivative in ethanol and water, which also can be used as a wetting agent for aqueous paints and coatings. The identity of the sulfosuccinate has not been disclosed. The product is claimed to have good wetting properties, no increase in foam and good recoatability. The surface tension is moderate. Application areas are decorative paints, wood and furniture coatings, automotive and repair coatings, industrial coatings, printing inks and overprint varnishes.

1. Health effects of sulfosuccinates

210. Toxicological information is scarce. Sulfosuccinates are irritants to eyes, skin and the respiratory system, especially upon prolonged or repeated contact. Dermatitis has been observed as a long-term effect, as have central nervous system depression and injury to the heart, the liver and blood-forming organs. The substance di(2-ethylhexyl) sulfosuccinate has low acute toxicity if swallowed (LD_{50} (oral, rat) = 1.9 g/kg).[156] Information found in the United States Government's Hazardous Substances Data Bank suggests that di(2-ethylhexyl) sulfosuccinate is mildly toxic

[153] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[154] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[155] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[156] UNEP/POPS/POPRC.8/INF/17/Rev.1.

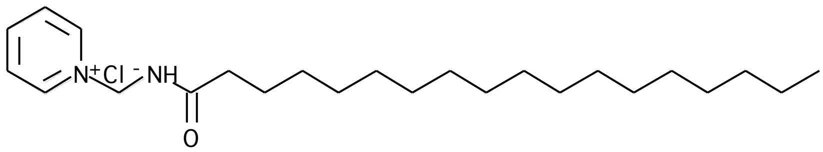
(upon ingestion) to humans, with a probable oral lethal dose (in humans) of 0.5–5 g/kg. A possible metabolite is the branched 2-ethylhexanol, which may have reproductive effects.

2. Environmental effects of sulfosuccinates

211. Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate; however, a $^{96h}LC_{50}$ value of 10–100 mg/l for *Leuciscus idus* (a small fresh-water cyprinoid fish) shows that the sulfosuccinate is harmful to aquatic organisms.[157] More information is needed in order to make an accurate assessment.

K. Stearamidomethyl pyridine chloride

212. A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, which was previously marketed by ICI as Velan PF:



213. The substance reacted 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. Pyridine might be evaluated differently now. Further information about its properties is lacking.

1. Health effects of stearamidomethyl pyridine chloride

214. Published data on this chemical are lacking.

2. Environmental effects of stearamidomethyl pyridine chloride

215. Published data on this chemical are lacking.

L. Polypropylene glycol ether, amines and sulfates

216. Possible replacements for fluorosurfactants in some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor® FAS 30 is the sodium salt of fatty alcohol polyglycol ether sulfates, which are preferentially used in the emulsion polymerization of acrylate and methacrylate esters, styrene and vinyl esters. These anionic emulsifiers are also combined with non-ionic Emulan® grades in order to achieve desired properties such as a particular particle size or emulsion stability. Because of their “foaming” properties, fatty alcohol polyglycol ether sulfates are also used in cosmetics and fire-fighting foams.

217. A fatty alcohol polyglycol ether sulfate has the following general formula:

$$RO(CH_2CH_2O)_nSO_3X$$

in which *R* represents a linear or branched alkyl and/or alkenyl group having, for example, 12 to 16 carbon atoms, *n* represents a number mainly from 2 to 4 and *X* represents a cation selected from the group consisting of sodium, ammonium or substituted ammonium.

218. A related non-fluorosurfactant is Enthone® (ethoxylated oleyl amine, CAS no. 26635-93-8), used in decorative chrome plating and in many other applications.[158] Its general formula is as follows:

$$R\text{-}N(CH_2CH_2O)_mH(CH_2CH_2O)_nH \qquad \text{(R: alkyl group)}$$

1. Health effects of polypropylene glycol ether, amines and sulfates

219. There is a lack of data on this chemical. Emulphor FAS 30 has low acute toxicity by ingestion (oral LD_{50}> 2 g/kg b.w.) and is not considered to be irritating. Enthone and other polyethylene glycol amines are non-toxic and non-irritating non-ionic emulsifiers.

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[157] UNEP/POPS/POPRC.8/INF/17/Rev.1.

[158] www.enthone.com/pwb/index.aspx

2. Environmental effects of polypropylene glycol ether, amines and sulfates

220. Emulphor FAS 30 is readily biodegradable (> 70% elimination according to the OECD biodegradation screening test (301E)) and does not seem to be acutely toxic to aquatic organisms, as the reported $^{96h}LC_{50}$ value for fish (*Leuciscus idus*) is > 100 mg/L. Enthone is readily degradable, with low toxicity. There is, however, a lack of data on these chemicals.

V. Comparative assessment of PFOS and possible alternatives

221. Comparative assessment of PFOS and its possible alternatives with regard to technical, socioeconomic, environmental, health and safety considerations is a very complex task requiring much more data and other information than are normally available. Often much more information is available about PFOS than about possible alternatives, which may be newly developed substances covered by patents and for which manufacturers have not provided information. For this reason rigid selection criteria are not useful; information on the alternatives will be scarcer, and it will be of lower scientific quality because much of it will be non-peer-reviewed.

222. In addition, if sufficient information is available then one may have to subjectively weigh short-term economic considerations and practical feasibility against long-term economic and safety considerations. None of the alternatives will be perfect and without hazards, but at least they should be less hazardous than PFOS. For example, fluorinated alternatives with fluorinated alkyl chains shorter than C_8may be less toxic and bioaccumulative but still persistent indefinitely in the environment.

223. It might be that the C_6-chemistry of fluorinated alternatives is not sufficiently safe. This is illustrated by the similar half-life of perfluorohexane sulfonate compared to PFOS in human blood. In addition, there is a growing body of observations of toxic effects in humans and animal studies and PFHxS is found seawater, animals, and humans in the Arctic. Furthermore, chemicals with fluorinated chains longer than C_8 seem to be more toxic and bioaccumulative than PFOS.

224. Further, in evaluating the technical properties, fitness for use and durability of the alternatives for each separate application, it is necessary to evaluate socio-economic considerations, including long-term costs due to environmental and health effects; differences between sectors, enterprises (including size), countries and regions; product importance; economic constraints; and social costs. The availability of alternatives seems to be the same worldwide, because the providers are mainly large international companies.

225. Economically useful data will probably also be scarce. In general, very little information about the prices of alternatives was found in the Danish survey[159] even though the producers of alternative products were asked specifically about such information. The information received, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. One company mentioned that the price of alternatives was intentionally kept at the same level as that of PFOS-related compounds. While it was impossible to obtain exact prices, in the coatings and paints area the non-fluorinated alternatives were found to be cheaper.

226. More recent information indicates that some alternatives may be priced comparably to one other but be more expensive than PFOS derivatives. Some price examples for laboratory chemicals are shown in table 7. The purity and prices of bulk materials may be lower.

Table 7: Prices of selected basic polyfluorinated laboratory chemicals[160]

Chemical	CAS no.	Molecular weight	Price in € per 100 g
Perfluorobutane sulfonyl fluoride (PFBSF)	375-72-4	303.09	136
Perfluorobutane sulfonic acid (PFBS)	59933-66-3	300.10	1,800
Perfluorooctane sulfonic acid (PFOS)	1763-23-1	500.13	1,122
Perfluorooctane sulfonyl fluoride (PFOSF)	307-35-7	502.12	92
Fluorotelomer 6:2 alcohol	647-42-7	364.10	130
Fluorotelomer 8:2 alcohol	678-39-7	464.12	187
Fluorotelomer 10:2 alcohol	865-86-1	564.14	1,440
Methyl nonafluorobutyl ether	163702-07-6	250.06	745

[159] Poulsen PB, Jensen AA, Wallström E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project 1013. Danish Environmental Protection Agency. www.mst.dk/Udgivelser/Publications/2005/06/87-7614-668-5.htm

[160] ABCR 2006–2007 catalogue: Fluorochemicals. Karlsruhe, Germany.

227. Although the table shows the opposite, C_6-fluorochemistry alternatives may often be more expensive than C_8-fluorochemistry alternatives, which are subject to a phase-out and therefore obsolete.

228. Especially at the beginning, alternatives might be more expensive to purchase or use; however, this possible short-term cost increase is balanced by eliminating a very hazardous and persistent chemical. The prices of substitutes will decrease in the long run with a growing market and increasing competition.

VI. Conclusions, recommendations and future developments

A. Low surface tension is a key function

229. In addition to stability, a key factor in the performance of fluorosurfactants is their extremely low surface tension, which currently cannot be matched with other surfactants. PFOS is the optimal substance with regard to that property. Owing to environmental and health concerns, however, surfactants without fluorine content could be used as alternatives if such low surface tension levels are not needed. Given the relatively high prices of fluorosurfactants, switching can in some cases also have economic benefits.

B. Substitutes for PFOS are available

230. Fluorinated or non-fluorinated alternatives exist for nearly all current uses of PFOS. While the alternatives may beinitially slightly more expensive and less effective, they will normally be less hazardous. In Japan only three essential applications are left for PFOS: 1) etching agent for semiconductors, 2) semiconductor resists and 3) photo films for industrial purposes.[161]

231. The most common PFOS alternatives in use are fluorotelomers, which are precursors for PFCA. Formerly, C_8-fluorotelomers were a frequent choice;they have been shown, however, to degrade into PFOA, which also has hazardous properties. For that reason the producers of fluorochemicals in the EU, Japan, and US have agreed with the United States Environmental Protection Agency to commit to working toward the elimination of PFOA, chemicals that breakdown to PFOA, and related higher homologues by 2015.[162] As a result, there has been a shift by these producers to C_6-, C_4- and C_3-perfluoroalkylated chemicals.

C. Need for better alternatives

232. For some uses non-fluorinated chemicals have been introduced as alternatives; examples include silicones, aliphatic alcohols and sulfosuccinates. It might also be that a particular use or product is no longer essential, or that a process could be changed to eliminate the need for PFOS, as has happened in the photographic industry and in chrome plating.

D. Need for incentives

233. There is a need for incentives to develop safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for their development. The international requirements applying to all parties to the Stockholm Convention, which must be implemented in national law, constitute one such incentive. Article 3 of the Stockholm Convention states that Parties with regulatory and assessment schemes for new chemical substances shall take measures to regulate with the aim of preventing the production and use of substances that exhibit characteristics of POPs. The development of national law is an important tool for promoting incentives to identify and use alternative substances and processes. Postponing the development of national law until perfect alternatives are available is not wise because manufacturers may not develop alternatives if they are not forced to do so.

E. Complex assessment

234. The fluoro chemistry is diverse and complex. There may therefore be a need for a mechanism for continuously updating information regarding the alternatives' substitution properties and hazards. Such a mechanism should be consistent with Article 9, subparagraph 1 (b), of the Convention which states that each Party shall facilitate or undertake the exchange of information relevant to alternatives

161 Presentation by Takashi Fukushima, Japanese Ministry of Economy, Trade and Industry, at the national workshop on nine new persistent organic pollutants subject to the Stockholm Convention and the implementation of the Convention in China, Beijing, 1–2 July 2010.

162 http://www.epa.gov/oppt/pfoa/pubs/stewardship

to persistent organic pollutants, including information relating to their risks as well as to their economic and social cost.

235. Assessment of the economic implications of switching to alternatives to PFOS rests on cost effectiveness considerations. . The cost effectiveness of different measures is expressed by the ratio of cost to the reduced load of hazardous substances. As there are large uncertainties, different scenarios – a worst case scenario (low load reduction effectiveness – high costs) and best case scenario (highload reduction effectiveness – low costs) - are used for the calculation of cost effectiveness. The quantitative assessment is complemented by a comprehensive qualitative evaluation to include sustainability aspects, which is mainly based on experts' estimates rather than on empirical data. Inclusion of life cycle considerations in the assessment may also be useful.[163] A major cost effectiveness study, funded by the European Commission, has been published for PFOS and PFOA.[164] There is no publicly available cost effectiveness study for other PFCs. Often available useful economic data may also be scarce and biased. The sparse information received to date, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. Specifically in the coatings and paints area, the non-fluorinated alternatives are cheaper.

F. Need for more public data and information on alternatives

236. Much fewer data are currently available publicly on the alternatives than on PFOS. Much of the information is from patent literature, and the identities of actual chemicals used are often not disclosed. This reinforces the need for implementation of paragraph 1 of Article 9 on the information exchange regarding alternatives to persistent organic pollutants.

237. Chemicals with structures similar to those of the listed PFOS substances could cause concerns similar to those related to the latter substances. This should be considered in evaluating alternatives. Increasing effort will be needed to study the toxicological and environmental properties of alternatives and to make the resulting information public and trustworthy by publishing it in peer reviewed scientific journals.

238. A strategic integrated approach to testing is needed to speed development of the data required to understand the issues and concerns relating to the various types of alternatives. According to the United States Environmental Protection Agency, testing can be done scientifically without necessarily testing every alternative chemical for every endpoint. The private sector has a key responsibility in this regard.

G. Need for better communication in the value chain

239. It is important that the issues associated with PFOS as a globally recognized persistent organic pollutant, including the health and environmental risks, be made fully known to suppliers and industries. Producers need to have better knowledge about the use of PFOS in processes, products and articles. It is also important to provide information to customers and consumers so that they can develop informed opinions about the possible need to change products or processes. Industries that are proactive in phasing out the use of a very hazardous chemical such as PFOS are likely to reap future market advantages.

H. Need for more international cooperation

240. PFOS and its substitutes are being studied and evaluated in parallel by authorities in many countries. More international cooperation and private sector transparency can save resources and speed up processes. The OECD Parallel Process for the Notification of New Chemicals is one useful approach (for new chemicals) to consider in developing international collaboration on assessing potential alternatives to PFOS and other polyfluorinated chemicals of concern.

[163] http://www.unep.fr/shared/publications/pdf/DTIx1208xPA-LifeCycleApproach-Howbusinessusesit.pdf

[164] Cohiba, control of hazardous substances in the Baltic sea region, guidance document 4, http://www.google.se/url?sa=t&rct=j&q=&esrc=s&frm=1&source=web&cd=1&ved=0CDEQFjAA&url=http%3A%2F%2Fwww.cohiba-project.net%2Fpublications%2Fen_GB%2Fpublications%2F_files%2F87107446768797277%2Fdefault%2FPFOA-PFOS.pdf&ei=MCInUdXqEuXd4QTyxYCoAw&usg=AFQjCNGF4ZVXK2Wy6mtcS0Cv31SOefClww&sig2=kXgiPktG2DJswuQF-BYyTw&bvm=bv.42768644,d.bGE

I. Other sources consulted

Bruinen de Bruin Y, Zweers P, Bakker J, Beekman M. 2009. Estimation of emissions and exposures to PFOS used in industry. A PFOS use inventory in metal plating and fire fighting. Bilthoven: RIVM Report 601780002.

Perfluorinated substances and their uses in Sweden. 2006. www.kemi.se/upload/Trycksaker/Pdf/Rapporter/Report7_06.pdf

PFOA in Norway. 2007. Survey of national sources, Report 2354, SFT. www.sft.no/publikasjoner/2354/ta2354.pdf

PFOS Regulatory Impact Analysis Statement. 2008. *Canada Gazette*, part II (Vol. 142, No. 12), 11 June 2008. www.ec.gc.ca/ceparegistry/documents/regs/g2-14212_rias1.pdf

2007 OECD workshop on perfluorocarboxylic acids (PFCAs) and precursorsreport 2007. www.olis.oecd.org/olis/2007doc.nsf/LinkTo/NT00002AB6/$FILE/JT03229256.PDF

Fluorosurfactants Conference. June 2008. http://pft.fh-fresenius.de/

OECD. [supply date] Perfluorooctane sulfonate (PFOS) and related chemical products. www.oecd.org/document/58/0,,en_2649_34375_2384378_1_1_1_1,00

Shuji Tamura presentation. 2008. "Substitution and alternatives". POPRC4, October 2008.

Ryo Usami presentation: 2008. "Case study on PFOS". POPRC4, October 2008.

Presentations at the International Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives, 12–13 February 2009, Geneva, Switzerland.

Overview of Existing Information on PFOS Production, Use, Emissions and Pathways to the Environment and Cost/Benefits with alternatives/substitutes. 25 January 2006.[165]

[165] www.unece.org/env/lrtap/TaskForce/popsxg/2006/Overview%20of%20existing%20information%20on%20PFOS%20emissions%20and%20pat.pdf

Appendix A

Reference list of recent publications on perfluorinated chemicals (PFCs)

Complementary to the reference list in UNEP/POPS/POPRC.8/INF/17/Rev.1

Emissions to and occurrence of PFCs into the environment

Ahrens, S. Felizeter, R. Sturm, Z. Xie, and R. Ebinghaus. Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. *Mar.Pollut Bull* 58 (9):1326-1333, 2009.

Bakke, T., Fjeld, E., Skaare, B., Berge. J.A., Green, N., Ruus, A., Schlabach, M., and Botnen, H. 2007. *Kartleg-ging av metaller og utvalgte nye organiske miljøgifter 2006. Krom, arsen, perfluoralkylstoffer, dikloretan, klorbenzener, pentaklorfenol, HCBD og DEHP.* SFT TA2284/2007. NIVA report 5464-2007. 105s.

Barber, J.L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., Jones, K.C. 2007. *Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. Journal of Environmental Monitoring*, 9 (6), 530-541.

Bytingsvik J, van Leeuwen SP, Hamers T, Swart K, Aars J, Lie E, Nilsen EM, Siig O, Derocher AE, Jenssen BM (2012) Perfluoroalkyl substances in polar bear mother-cub pairs: a comparative study based on plasma levels from 1998 and 2008, Environ Int 49:92-99

Björklund, J.A., Thuresson, K., De Wit, C.A. 2009. *Perfluoroalkyl compounds (PFCs) in indoor dust: Concentrations, human exposure estimates, and sources. Environmental Science and Technology*, 43 (7), 2276-2281.

Bossi, R., Riget, F.F., Dietz, R. 2005. *Temporal and spatial trends of perfluorinated compounds in ringed seal (Phoca hispida) from Greenland. Environmental Science and Technology*, 39 (19), 7416-7422.

Bossi, R., Riget, F.F., Dietz, R., Sonne, C., Fauser, P., Dam, M., Vorkamp, K. 2005. *Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands. Environmental Pollution*, 136 (2), 323-329.

Bossi, R., Strand, J., Sortkjær, O., Larsen, M.M. 2008. *Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. Environment International*, 34 (4), 443-450.

Butt, C.M., Berger, U., Bossi, R., Tomy, G.T. 2010. *Levels and trends of poly- and perfluorinated compounds in the arctic environment. Science of the Total Environment*, 408 (15), 2936-2965.

C. Eschauzier, J. Haftka, P. J. Stuyfzand, and Voogt P. de. Perfluorinated compounds in infiltrated river rhine water and infiltrated rainwater in coastal dunes. Environ.Sci.Technol. 44 (19):7450-7455, 2010.

Dinglasan-Panlilio, M. J. A., Mabury, S. A. 2006. *Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials. Environmental Science and Technology*. 40, 1447-1453.

Eschauzier C, Haftka J, Stuyfzand PJ, de Voogt P, Environ Sci Technol. Perfluorinated compounds in infiltrated river rhine water and infiltrated rainwater in coastal dunes. 2010 Oct 1;44(19):7450-5.

Fjeld, E., Schlabach, M., Berge J.A., Green, N., Eggen, T., Snilsberg, P., Vogelsang, C., Rognerud, S., Kjellberg, G., Enge, E.K., Dye, C.A., Gundersen, H. 2005. *Kartlegging av utvalgte nye organiske miljøgifter 2004. Bromerte flammehemmere, perfluoralkylstoffer, irgarol, diuron, BHT og dicofol*, NIVA rapport nr 5011-2005.

Galatius, A., Dietz, R., Rigét, F.F., Sonne, C., Kinze, C.C., Lockyer, C., Bossi, R. 2011. *Temporal and life history related trends of perfluorochemicals in harbor porpoises from the Danish North Sea. Marine Pollution Bulletin*, 62 (7), 1476-1483.

Haug, L.S., Huber, S., Becher, G., Thomsen, C. 2011b. *Characterisation of human exposure pathways to perfluorinated compounds - Comparing exposure estimates with biomarkers of exposure. Environment International*, 37 (4), 687-693.

Haug, L.S., Huber, S., Schlabach, M., Becher, G., Thomsen, C. 2011. *Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes. Environmental Science and Technology*, 45 (19), 7991-7998.

Haukås, M., Berger, U., Hop, H., Gulliksen, B., Gabrielsen, G.W. 2007. *Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. Environmental Pollution*, 148 (1), 360-371.

Huber, S., Haug, L.S., Schlabach, M. 2011. *Per- and polyfluorinated compounds in house dust and indoor air from northern Norway - A pilot study. Chemosphere*, 84 (11), 1686-1693.

Huset CA, Barlaz MA, Barofsky DF, Field JA, 2011, Quantitative determination of fluorochemicals in municipal landfil leachates, Chemosphere 82:1380-1386V. Gellrich, T. Stahl, and T. P. Knepper. Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere, 2012.

Jahnke, A., Huber, S., Temme, C., Kylin, H., Berger, U. 2007. *Development and application of a simplified sampling method for volatile polyfluorinated alkyl substances in indoor and environmental air. Journal of Chromatography A*, 1164 (1-2).

Kallenborn, R., Berger, U., Järnberg, U., Dam, M., Glesne, O., Hedlund, B. 2004. *Perfluorinated alkylated substances (PFAS) in the Nordic environment*. Nordic Council of Ministers.

Lin AY, Panchangam SC, Lo CC (2009) The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers.Environ Pollut. 2009 Apr;157(4):1365-72. doi: 10.1016/j.envpol.2008.11.033. Epub 2008 Dec 30.

Loi EI, Yeung LW, Mabury SA, Lam PK (2013) Environ Sci Technol **DOI:** 10.1021/es303805k

Löfstrand, K., Jörundsdóttir, H., Tomy, G., Svavarsson, J., Weihe, P., Nygård, T., Bergman, Å. 2008. *Spatial trends of polyfluorinated compounds in guillemot (Uria aalge) eggs from North-Western Europe. Chemosphere*, 72 (10), 1475-1480.

Miljeteig, C., Strøm, H., Gavrilo, M.V., Volkov, A., Jenssen, B.M., Gabrielsen, G.W. 2009. *High levels of contaminants in ivory gull Pagophila eburnea eggs from the Russian and Norwegian arctic. Environmental Science and Technology*, 43 (14), 5521-5528.

P. J. Lasier, J. W. Washington, S. M. Hassan, and T. M. Jenkins. Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus. Environ.Toxicol.Chem., 2011.

Report number TA-2354/2007. Norwegian Pollution Control Authority, Survey of National Sources, 2007.

Report *number TA*-2367/2008*. Green, N., Schlabach, M., Bakke, T., Brevik, E.M., Dye, C., Herzke, D. Screening of selected metals and new organic contaminants 2007. Norwegian Pollution Control Authority, Oslo, Norway*.

Report *number TA*-2444/2008*. Green, N., Schlabach, M., Bakke, T., Brevik, E.M., Dye, C., Herzke, D.* 2008. *Screening of polyfluorinated organic compounds at four fire training facilities in Norway. Norwegian Pollution Control Authority, Oslo, Norway*. *Norwegian Pollution Control Authority, Oslo, Norway*.

Report number TA-3005-2012. 2012. *Noen miljøskadelige stoffer i avløpsslam –forekomst og miljørisiko,*

Smithwick, M., Mabury, S.A., Solomon, K.R., Sonne, C., Martin, J.W., Born, E.W., Dietz, R., Derocher, A.E., Letcher, R.J., Evans, T.J., Gabrielsen, G.W., Nagy, J., Stirling, I., Taylor, M.K., Muir, D.C.G. 2005. *Circumpolar study of perfluoroalkyl contaminants in polar bears (Ursus maritimus). Environmental Science and Technology*, 39 (15), 5517-5523.

Telomer Research Program 2002. Telomer Research Program Update, Presented to the USEPA OPPT, November 25, 2002; U.S. Environmental Protection Agency public docket AR226-1141.

T. Meyer, A. O. De Silva, C. Spencer, and F. Wania. Fate of perfluorinated carboxylates and sulfonates during snowmelt within an urban watershed. Environ Sci.Technol. 45 (19):8113-8119, 2011.

Theobald, N., Gerwinski, W., Caliebe, C., Haarich, M. 2007. *Development and validation of a method for the determination of polyfluorinated organic substances in sea water, sediments and biota.* Occurrence of these compounds in the North and Baltic Seas, Umweltbundesamt.

Verreault, J., Berger, U., Gabrielsen, G.W. 2007. *Trends of perfluorinated alkyl substances in herring gull eggs from two coastal colonies in northern Norway*: 1983-2003. *Environmental Science and Technology*, 41 (19), 6671-6677.

V. Gellrich, T. Stahl, and T. P. Knepper. Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere, 2012´

Yan H, Zhang CJ, Zhou Q, Chen L, Meng XZ (2012) Short- and long-chained perfluorinated acids in sewage sludge from Shanghai, China, Chemosphere 88:1300-1305

Zhang W, Zhang Y, Taniyasu S, Yeung LWY, Lam PKS, Wang J, Li X, Yamashta N, Dai J (2012) Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants ineconomically developed areas of China, Environ Pollut 176:10-17

Zhao Z, Xie Z, Moller 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

Xu Z, Fiedler S, Pfister G, Henkelmann B, Mosch C, Volkel W, Fromme H, Schramm KW (2013) Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany, Sci Total Environ 443:485-490

Modelling of emissions to the environment

Bennett, D.H., McKone, T.E., Matthies, M., Kastenberg, W.E., 1998. *General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment.* Environmental Science & Technology 32 (24), 4023-4030.

Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. *Assessing long-range transport potential of persistent organic pollutants.* Environmental Science & Technology 34 (4), 699-703.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. *Towards a global historical emission inventory for selected PCB congeners - A mass balance approach.* 3. An update. Science of the Total Environment 377 (2-3), 296-307.

Breivik, K., Wania, F., Muir, D.C.G., Alaee, M., Backus, S., Pacepavicius, G., 2006. *Empirical and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether*. Environmental Science & Technology 40 (15), 4612-4618.

Pistocchi, A., Loos, R., 2009. *A map of European emissions and concentrations of PFOS and PFOA*. Environmental Science and Technology 43 (24), 9237-9244.

Wania, F., 2006. *Potential of degradable organic chemicals for absolute and relative enrichment in the arctic.* Environmental Science & Technology 40 (2), 569-577.

Wania, F., Mackay, D., 1996. Tracking the distribution of persistent organic pollutants. Environmental Science & Technology 30 (9), A390-A396.

Food and drinking water

Clarke, D.B., Bailey, V.A., Routledge, A., Lloyd, A.S., Hird, S., Mortimer, D. N., Gem, E.M. 2010. *Dietary intake estimate for perfluorooctanesulphonic acid (PFOS) and other perfluorocompounds (PFCs) in UK retail foods following determination using standard addition LC-MS/MS.* Food Additives and Contaminants, 27, 4, 530-545.

Eschauzier C, Beerendonk E, Scholte-Veenendaal P, De Voogt P (2012) Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain, Environ Sci Technol 46:1708-1715

Falandysz, J., Taniyasu, S., Gulkowska, A., Yamashita, N. and Schulte-Oehlmann, U. 2006. *Is fish a major source of fluorinated surfactants and repellents in human living on the Baltic coast*. Environ. Sci. Technol., 40, 748-751.

Fromme, H., Schlummer, M., Möller, A., Gruber, L., Wolz, G., Ungewiss, J., Böhmer, S., Dekant, W., Mayer, R., Liebl, B. and Twardella, D. 2007. *Exposure of an adult population to perfluorinated substances using dublicate diet portions and biomonitering data.* Environ. Sci. Technol., 41, 7928-7933.

Granby, K., Technical University of Denmark. 2012. *PFCs in Danish fish and animal food* (not published data).

Gebbink WA, Ullah S, Sandblom O, Berger U (2013) Polyfluoroalkyl phosphate esters and perfluoroalkyl carboxylic acids in target food samples and packaging-method development and screening, Environ Sci Pollut Res Int

Haug, L.S., Salihovic, S., Jogsten, I.E., Thomsen, C., van Bavel, B., Lindström, G., Becher, G. 2010a. *Levels in food and beverages and daily intake of fluorinated compounds in Norway*. Chemosphere, 80, 1137-1143.

Haug, L.S., Thomsen, C., Brantsæter, A.L., Kvalem, H.E., Haugen, M., Becker, G., Alexander, J., Meltzer, H.M., Knutsen, H.K. 2010b. *Diet and particulary seafood are major sources of perfluorinated compounds in humans.* Environment International, 36, 772-778.

Haug LS, Thomsen C, Brantsæter AL, Kvalem HE, Haugen M, Becher G, Alexander J, Meltzer HM and Knutsen HK. 2010. Diet and particularly seafood are major sources of perfluorinated compounds in humans. Environ. Int. 36, 772-778.

Hölzer, J., Midasch, O., Rauchfuss, K., Kraft, M., Reupert, R., Angerer, J., Kleeschulte, P., Marschall, N. and Wilhelm, M. 2008. *Biomonitering of perfluorinated compounds in children and adults exposed to perfluooctanoate-contaminated drinking water,* Environmental Health Perspectives, vol 116 (5), 651-657.

Mons, M., van Roon, A., de Voogt, P. 2007. *Perfluoroalkylated substances in Dutch drinking water sources*, KIWA water, BTO 07.048, Nieuwegein, 2007.

Rylander, C., Brustad, M., Falk, H., Sandanger, T. M. 2009. *Dietary predictors and plasma concentartions of pefluorinated compounds in a costal population from Nothern Norway.* Jour of Environmental and Public Health, vol 2009, Article ID 268219, 10 pages.

Schuetze, A., Heberer, T., Effkemann, S., Juergensen, S., 2010. *Occurrence and assessment of perfluorinated chemicals in wild fish from Nothern Germany*. Chemosphere, 78, 647-652.

Skutlarek, D., Exner, M., Farber, H. 2006. *Perfluoinated surfactants in surface and drinking water.* Environ Sci Pollut Res Int, vol 13 (5), 299-307.

Tittlemier, S.A., Pepper, K., Edwards, L. 2006. *Concentrations of perfluorooctanesulfonamides in Canadian Total Diet Study composite food samples collected between 1992-2004*. J. Agric Food Chem, 54, 8385-8389.

Trier, X. 2011. *Polyfluorinated surfactants in food packaging of paper and board.* Ph.D. thesis.

Trier, X. at al., 2011. *Polyfluorinated surfactants (PFS) in paper and board coatings for food pakaging*. Environ Sci Pollut Res, 18, 1108-1120.

Trier, X., Pedersen, G. A., Granby, K. 2012. *A Danish survey: Screening of fluorinated substances in food contact materials of paper and board* (results not yet publiched).

Trudel, D., Horowitz, L., Wormuth, M., Scheringer, M., Cousins, I. T. and Hunderbühler, K. 2008. *Estmating Consumer Exposure to PFOS and PFOA.* Risk Analysis, Vol 28, 2, 251–269.

Ullah, S., Alsberg, T., Berger, U., 2011. *Simultaneous determination of perfluoroalkyl phosphonates, caboxylates and sulfonates in drinking water*. Jour of Chromatography A, 1218, 6388-6395.

Vestergren, R., Cousins, I.T., Trudel, D., Wormuth, M. and Scheringer, M. 2008. *Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA*. Chemosphere 73, 1617-1624.

Vestergren, R., Cousins, I.T. 2009. *Tracking the Pathways of Human Exposure to Perfluorocarboxylates*. Environmental Science & Technology 43 (15), 5565-5575.

Consumer products

3M. 2010. *Scotchgard Carpet & Rug protector (1023-17N).* Material safety data sheet.

Barber, J.L., Berger, U., Chaemfa, C., Huber, S., Jahnke, A., Temme, C., Jones, K. 2007. *Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe.* J. Environ. Monitor, 9, 530-541.

Berger, U., Herzke, D. 2006. *Per- and polyfluorinated alkyl substances (PFAS) extracted from textile samples*. Organohalogen compounds, 68, 2023-2026.

Castro, I.C., Briceno, J.C. 2010. *Perfluorocarbon-based oxygen carriers: Review of Products and trials.* Artif. organs, 34, 622-634.

Cinglasan-Panlilio, M.J.A., Mabury, S.A. 2006. *Significant residual fluorinated alcohols present in various fluorinated materials*. Environ. Sci. Technol., 40, 1447-1453.

De Silva AO, Allard CN, Spencer C, Webster GM, Shoeib M (2012) Phosphorus-containing fluorinated organics: polyfluoroalkyl phosphoric acid diesters (diPAPs),

DuPont. 2004. *DuPont Teflon Advanced carpet and upholstery protection.* Usage information.

DuPont. 2005. *Teflon Advanced*. Safety Data Sheet.

Fraser, A.J., Webster, T.F., Watkins, D.F., Nelson, J.W., Stapelton, H.J., Calafat, A.M., Kato, K., Shoeib, M., Vieria, V.M., McClean, M.D. 2012. *Polyfluorinated compounds in serum linked to indoor air in office environments.* Environ. Sci. Technol., 46, 1209-1215.

Gelest. 2005. *SiBRID fluorocarbon silicone.* Product information.

Goosey, E., Harrad, S. 2011. *Perfluoroalkyl compounds in dust from Asian, Australian, European, and North American homes and UK cars, classrooms, and offices*. Environ. Int., 37, 86–92.

Goosey, E., Harrad, S. 2012. *Perfluoroalkyl substances in UK indoor and outdoor air: Spatial and seasonal variation, and implications for human exposure.* Environ. Int., 45, 86–90.

Haug, L.S., Huber, S., Schlabach, M., Becher, G., Thomsen, C. 2011. *Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes.* Environ. Sci. Technol., 45, 7991–8.

Herzke, D., Olsson, E., Posner, S. 2012. *Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway - A pilot study*. Chemosphere, 88, 980-987.

Huber, S., Haug, L.S., Schlabach, M. 2011. *Per- and polyfluorinated compounds in house dust and indoor air from northern Norway — a pilot study.* Chemosphere, 84, 1686–93.

Jahnke, A., Ahrens, L., Ebinghaus, R., Temme, C. 2007. *Urban versus remote air concentrations of fluorotelomer alcohols and other perfluorinated alkyl substances in Germany*. Environ. Sci. Technol., 41, 745-752

Jensen, A.A., Poulsen, P.B., Bossi, R. 2008. *Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, No. 99*. Danish Environmental Protection Agency.

Jogsten, I.E., Nadal, M., van Bavel, B., Lindström, G., Domingo, J.L. 2012. *Per- and polyfluorinated compounds (PFCs) in house dust and indor air in Catalonia Spain: Implications for human exposure*. Environ. Int., 39, 172-180.

Kato, K., Calafat, A.M., Needham, L.L. 2009. *Polyfluoroalkyl chemicals in house dust.* Environ. Res., 109, 518–23.

Key, B.D., Howell, R.D., Criddle, C.S. 1997. *Fluorinated organics in the biosphere.* Environ. Sci. Technol., 31, 2445-2454.

Kim, S.K., Shoeib, M., Kim, K.S., Park, J.E. 2012. *Indoor and outdoor poly- and perfluoroalkyl substances (PFASs) in Korea determined by passive air sampler.* Environ. Pollut., 162, 144-150.

Langer, V., Dreyer, A., Ebinghaus, R. 2010. *Polyfluorinated compounds in residential and nonresidential indoor air.* Environ. Sci. Technol., 44, 8075–81.

Liu, W., Takahashi, S., Sakuramachi, Y., Harada, K.H., Koizumi, A. 2012. *Polyfluorinated telomers in indoor air of Japanese houses*. Chemosphere, In press.

Moe, M.K., Huber, S., Svenson, J., Hagenaars, A., Pabon, M., Trümper, M., Berger, U., Knapen, D., Herzke, D. 2012. *The structure of the fire fighting foam surfactant Forafac1157 and its biological and photolytic transformation products*. Chemosphere, 89, 869–875.

Rosenmai AK, Nielsen FK, Pedersen M, Hadrup N, Trier X, Christensen JH, Vinggaard AM (2013) Fluorochemicals used in food packaging inhibit male sex hormone synthesis, Toxicol Appl Pharmacol 266:132-142

Shoeib, M., Harner, T., Ikonomou, M., Kannan, K. 2004. *Indoor and outdoor air concentrations and phase partitioning of perfluoroalkylsulfonamides and polybrominated diphenyl ethers.* Environ. Sci. Technol., 38, 131-1320.

Shoeib, M., Harner, T., Webster, G.M., Lee, S.C. 2011. *Indoor sources of poly- and perfluorinated compounds (PFCs) in Vancouver, Canada: implications for human exposure.* Environ. Sci. Technol., 45, 7999–8005.

Shoeib, M., Harner, T., Zhu, J. 2007. *Indoor air & dust concentrations of fluorotelomer alcohols.* Organohalogen Compounds, 69, 146-149.

Shoeib, M.,Harner, T., Wilford, B.H., Jones, K.C., Zhu, J. 2005. *Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: Occurence, partitioning, and human exposure*. Environ. Sci. Technol., 39, 6599-6606.

Sinclair, E., Kim, S.K., Akinleye, H.B., Kannan, K. 2007. *Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags*. Environ. Sci. Technol., 41, 1180-1185.

Strynar, M.J., Lindstrom, A.B. 2008. *Perfluorinated compounds in house dust from Ohio and North Carolina, USA*. Environ. Sci. Technol., 42, 3751–6.

Vorob'ev, S.I. 2009. *First- and second-generation perfluorocarbon emulsions.* Pharm. Chem. J.-USSR, 43, 30-40.

Yang, Z., Price, C., Bosco, G., Tucci, M., El-Badri, N.S., Mangar, D., Camporesi, E.M. 2008. *The effect of isovolemic hemodilution with Oxycyte, a perfluorocarbo emulsion, on cerebral blood flow in rats.* PLOS one, 3, 1-5.

Zaggia, A., Ameduri, B. 2012. *Recent advances on synthesis of potentially non-bioaccumulable fluorinated sufractants*. Current Opinion in Colloid & Interface Science, 17, 188-195.

Occurrence of PFCs in human

Antignac JP, Veyrand B, Kadar H, Marchand P, Oleko A, Bizec BL, Vandentorren S (2013) Occurrence of perfluorinated alkylated substances in breast milk of French women and relation with socio-demographical and clinical parameters: Results of the ELFE pilot study, Chemosphere

Bonefeld-Jorgensen, E.C., Long, M., Bossi, R., Ayotte, P., Asmund, G., Kruger, T., Ghisari, M., Mulvad, G., Kern, P., Nzulumiki, P., Dewailly, E. 2011. *Perfluorinated compounds are related to breast cancer risk in Greenlandic Inuit: a case control study*. Environ Health 10, 88.

Cassone C, Taylor J, O'Brien J, Williams A, Yauk C, Crump D, Kennedy S Toxicol Sci. 2012 Jul 12. [Epub ahead of print] Transcriptional profiles in the cerebral cortex of chicken embryos following in ovo perfluorohexane sulfonate exposure.

Corsini E, Sangiovanni E, Avogadro A, Galbiati V, Viviani B, Marinovich M, Galli CL, Dell'Agli M, Germolec DR, Toxicol Appl Pharmacol. 2012 Jan 15;258(2):248-55. Epub 2011 Nov 18.

In vitro characterization of the immunotoxic potential of several perfluorinated compounds (PFCs).

D'Eon, J.C., Crozier, P.W., Furdui, V.I., Reiner, E.J., Libelo, E.L., Mabury, S.A. 2009. *Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers*. Environmental science & technology 43, 4589-4594.

Dinglasan, M.J., Ye, Y., Edwards, E.A., Mabury, S.A. 2004. *Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids.* Environmental science & technology 38, 2857-2864.

Ehresman, D.J., Froehlich, J.W., Olsen, G.W., Chang, S.C., Butenhoff, J.L. 2007. *Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals*. Environmental research 103, 176-184.

Fei, C., McLaughlin, J.K., Tarone, R.E., Olsen, J. 2007. *Perfluorinated chemicals and fetal growth: a study within the Danish National Birth Cohort.* Environ Health Perspect 115, 1677-1682.

Fraser, A.J., Webster, T.F., Watkins, D.J., Nelson, J.W., Stapleton, H.M., Calafat, A.M., Kato, K., Shoeib, M., Vieira, V.M., McClean, M.D. 2012. *Polyfluorinated compounds in serum linked to indoor air in office environments.* Environmental science & technology 46, 1209-1215.

Freberg, B.I., Haug, L.S., Olsen, R., Daae, H.L., Hersson, M., Thomsen, C., Thorud, S., Becher, G., Molander, P., Ellingsen, D.G. 2010 *Occupational exposure to airborne perfluorinated compounds during professional ski waxing.* Environ Sci Technol 44, 7723-7728.

Fromme, H., Tittlemier, S.A., Völkel, W., Wilhelm, M., Twardella, D. 2009. *Perfluorinated compounds – Exposure assessment for the general population in western countries*. Int J Hyg Environ Health 212, 239-270.

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.

Gutzkow, K.B., Haug, L.S., Thomsen, C., Sabaredzovic, A., Becher, G., Brunborg, G. 2012. *Placental transfer of perfluorinated compounds is selective--a Norwegian Mother and Child sub-cohort study*. Int J Hyg Environ Health 215, 216-219.

Halldorsson, T.I., Fei, C., Olsen, J., Lipworth, L., McLaughlin, J.K., Olsen, S.F. 2008. *Dietary predictors of perfluorinated chemicals: a study from the Danish National Birth Cohort*. Environ Sci Technol 42, 8971-8977.

Hanssen L, Röllin H, Odland JØ, Moe MK, Sandanger TM, J Environ Monit. 2010 Jun;12(6):1355-61. Epub 2010 Apr 28.Perfluorinated compounds in maternal serum and cord blood from selected areas of South Africa: results of a pilot study.

Hanssen L, Dudarev AA, Huber S, Odland JO, Nieboer E, Sandanger TM (2013) Partition of perfluoroalkyl substances (PFASs) in whole blood and plasma, assessed in maternal and umbilical cord samples from inhabitants of arctic Russia and Uzbekistan, Sc Total Environ doi: 10.1016/j.scitotenv.2013.01.029

Haug, L.S., Huber, S., Becher, G., Thomsen, C. 2011. *Characterisation of human exposure pathways to perfluorinated compounds--comparing exposure estimates with biomarkers of exposure*. Environ Int 37, 687-693.

Haug, L.S., Thomsen, C., Becher, G. 2009. *Time trends and the influence of age and gender on serum concentrations of perfluorinated compounds in archived human samples. E*nviron Sci Technol 43, 2131-2136.

Hoffman K, Webster TF, Weisskopf MG, Weinberg J, Vieira VM, Environ Health Perspect. 2010 Dec;118(12):1762-7. Epub 2010 Jun Exposure to polyfluoroalkyl chemicals and attention deficit/hyperactivity disorder in U.S. children 12-15 years of age.

Joensen, U.N., Bossi, R., Leffers, H., Jensen, A.A., Skakkebaek, N.E., Jorgensen, N. 2009. *Do perfluoroalkyl compounds impair human semen quality?* Environ Health Perspect 117, 923-927.

Jones, P.D., Hu, W., De Coen, W., Newsted, J.L., Giesy, J.P. 2003 *Binding of perfluorinated fatty acids to serum proteins.* Environ Toxicol Chem 22, 2639-2649.

Karrman, A., Ericson, I., van Bavel, B., Darnerud, P.O., Aune, M., Glynn, A., Lignell, S., Lindstrom, G. 2007a. *Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996-2004, in Sweden.* Environ Health Perspect 115, 226-230.

Karrman, A., Langlois, I., van Bavel, B., Lindstrom, G., Oehme, M. 2007b. *Identification and pattern of perfluorooctane sulfonate (PFOS) isomers in human serum and plasma*. Environ Int 33, 782-788.

Karrman, A., van Bavel, B., Jarnberg, U., Hardell, L., Lindstrom, G. 2006. *Perfluorinated chemicals in relation to other persistent organic pollutants in human blood*. Chemosphere 64, 1582-1591.

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.

Kubwabo C, Kosarac I, Lalonde K (2013) Determination of selected perfluorinated compounds and polyfluoralkyl phosphate surfactants in human milk, Chemosphere doi: 10.1016/j.chemosphere.2013.02.011

Lau, C. 2012. *Perfluoroalkyl acids: Recent research highlights*. Reprod Toxicol 33, 405-409.

Lee, H., Mabury, S.A. 2011. *A pilot survey of legacy and current commercial fluorinated chemicals in human sera from United States donors in 2009.* Environmental science & technology 45, 8067-8074.

Lee Yj, Kim MK, Bae J, Yang JH (2013) Concentrations of perfluoroalkyl compounds in maternal and umbilical cord sera and birth outcomes in Korea, Chemosphere 90:1603-1609

Lindh, C.H., Rylander, L., Toft, G., Axmon, A., Rignell-Hydbom, A., Giwercman, A., Pedersen, H.S., Goalczyk, K., Ludwicki, J.K., Zvyezday, V., Vermeulen, R., Lenters, V., Heederik, D., Bonde, J.P., Jonsson, B.A. 2012. *Blood serum concentrations of perfluorinated compounds in men from Greenlandic Inuit and European populations.* Chemosphere 88, 1269-1275.

Liu J, Li J, Luan Y, Zhao Y, Wu Y, Environ Sci Technol. 2009 Jun 1;43(11):4044-8.

Geographical distribution of perfluorinated compounds in human blood from Liaoning province, China.

Long, M., Bossi, R., Bonefeld-Jorgensen, E.C. 2012. *Level and temporal trend of perfluoroalkyl acids in Greenlandic Inuit.* Int J Circumpolar Health 71, 17998.

Needham, L.L., Grandjean, P., Heinzow, B., Jørgensen, P.J., Nielsen, F., Patterson, D.G., Sjödin, A., Turner, W.E., Weihe, P. 2010. *Partition of Environmental Chemicals between Maternal and Fetal Blood and Tissues*. Environ Sci Technol 45, 1121-1126.

Nilsson, H., Karrman, A., Rotander, A., van Bavel, B., Lindstrom, G., Westberg, H. 2010a. *Inhalation exposure to fluorotelomer alcohols yield perfluorocarboxylates in human blood?* Environ Sci Technol 44, 7717-7722.

Nilsson, H., Karrman, A., Westberg, H., Rotander, A., van Bavel, B., Lindstrom, G. 2010b. *A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax*. Environ Sci Technol 44, 2150-2155.

Nilsson, S., Makela, S., Treuter, E., Tujague, M., Thomsen, J., Andersson, G., Enmark, E., Pettersson, K., Warner, M., Gustafsson, J.A. 2001. *Mechanisms of estrogen action.* Physiol Rev 81, 1535-1565.

Rylander, C., Brustad, M., Falk, H., Sandanger, T.M. 2009. *Dietary predictors and plasma concentrations of perfluorinated compounds in a coastal population from northern Norway.* J Environ Public Health 2009, 268219.

Rylander C, Phi DT, Odland JO, Sandanger TM (2009) Perfluorinated compounds in delivering women from south central Vietnam, J Environ Monit 11:2002-2008

Rotander, Anna et al.; *Increasing levels of long-chain perfluorocarboxylic acids (PFCAs) in Arctic and North Atlantic marine mammals,* 1984–2009, Chemosphere, Volume 86, Issue 3, January 2012. Pages 278-285.

Schecter A, Malik-Bass N, Calafat AM, Kato K, Colacino JA, Gent TL, Hynan LS< Harris TR, Malla S, Birnbaum L (2012) Polyfluoroalkyl compounds in Texas children fom birth through 12 years of age, Environ Health Perspect 120:590-594

Strynar MJ, Lindstrom AB, Environ Sci Technol. 2008 May 15;42(10):3751-6.

Perfluorinated compounds in house dust from Ohio and North Carolina, USA.

Tiido, T., Rignell-Hydbom, A., Jonsson, B.A., Giwercman, Y.L., Pedersen, H.S., Wojtyniak, B., Ludwicki, J.K., Lesovoy, V., Zvyezday, V., Spano, M., Manicardi, G.C., Bizzaro, D., Bonefeld-Jorgensen, E.C., Toft, G., Bonde, J.P., Rylander, L., Hagmar, L., Giwercman, A. 2006. *Impact of PCB and p,p'-DDE contaminants on human sperm Y:X chromosome ratio: studies in three European populations and the Inuit population in Greenland.* Environ Health Perspect 114, 718-724.

Toms LM, Calafat AM, Kato K, Thompson J, Harden F, Hobson P, Sjodin A, Mueller JF (2009) Polyfluoroalkyl chemicals in pooled blood serum from infants, children, and adults in Australia, Environ Sci Technol 43:4194-4199

Thomsen C, Haug LS, Stigum H, Frøshaug M, Broadwell SL and Becher G. 2010. Changes in concentrations of perfluorinated compounds, polybrominated diphenyl ethers and polychlorinated biphenyls in Norwegian breast-milk during twelve months of lactation. *Environ. Sci. Technol.* 44, 9550-9556.

Wan HT, Leung PY, Zhao YG, Wei X, Wong MH, Wong CK (2013) Blood plasma concentrations of endocrine disrupting chemials in Hong Kong populations, J Hazard Mater pii: S0304-3894(13)00052-6

Vestergaard, S., Nielsen, F., Andersson, A.M., Hjollund, N.H., Grandjean, P., Andersen, H.R., Jensen, T.K. 2012. *Association between perfluorinated compounds and time to pregnancy in a prospective cohort of Danish couples attempting to conceive.* Hum Reprod 27, 873-880.

Weihe, P., Kato, K., Calafat, A.M., Nielsen, F., Wanigatunga, A.A., Needham, L.L., Grandjean, P. 2008. *Serum concentrations of polyfluoroalkyl compounds in Faroese whale meat consumers.* Environ Sci Technol 42, 6291-6295.

Wan HT, Leung PY, Zhao YG, Wei X, Wong MH, Wong CK (2013) Blood plasma concentrations of endocrine disrupting chemials in Hong Kong populations, J Hazard Mater pii: S0304-3894(13)00052-6

Yeung LW, Robinson S, Koschorreck J, Mabury SA (2013) Part 1. A temporal study of PFCAs and its precursors in human plasma from two German cities 1982 – 2009, Environ Sci Technol, DOI: 10.1021/es303716k

Human toxicity and environmental effects

(ECHA), E.C.A., 2008. *Summary Of Classification and Labelling: Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)* - PFOS. vol. 2012.

(ECHA), E.C.A., 2011. *Opinions of the Committee for Risk Assessment on proposals for harmonised classification and labelling* - PFOA. vol. 2012.

(ECHA), E.C.A., 2012a. Registry of current Harmonised Classification and Labelling intentions: heptadecafluorodecanoic acid. vol. 2012.

(ECHA), E.C.A., 2012b. *Registry of current Harmonised Classification and Labelling intentions: nonadecafluorononanoic acid*. vol. 2012.

Abbott, B.D., Wolf, C.J., Schmid, J.E., Das, K.P., Zehr, R.D., Helfant, L., Nakayama, S., Lindstrom, A.B., Strynar, M.J., Lau, C., 2007. *Perfluorooctanoic acid induced developmental toxicity in the mouse is dependent on expression of peroxisome proliferator activated receptor-alpha.* Toxicol Sci 98, 571-581.

Apelberg, B.J., Witter, F.R., Herbstman, J.B., Calafat, A.M., Halden, R.U., Needham, L.L., Goldman, L.R., 2007. *Cord serum concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in relation to weight and size at birth.* Environ Health Perspect 115, 1670-1676.

Bao J, Liu W, Lui L, Jin Y, Dai J, Ran X, Zhang Z, Tsuda S (2011) Perfluorinated compounds in the environment and the blood of residents living near fluorochemical plants in Fuxin, China, Environ Sci Technol 45:8075-8080

Begley, T.H., White, K., Honigfort, P., Twaroski, M.L., Neches, R., Walker, R.A., 2005. *Perfluorochemicals: potential sources of and migration from food packaging.* Food additives and contaminants 22, 1023-1031.

Beesoon S, Genuis SJ, Benskin JP, Martin JW (2012) Environ Sci Technol 46:12960-12967

Bennett, D.H., McKone, T.E., Matthies, M., Kastenberg, W.E., 1998. *General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment.* Environ Sci Technol 32, 4023-4030.

Benninghoff, A.D., Bisson, W.H., Koch, D.C., Ehresman, D.J., Kolluri, S.K., Williams, D.E., 2011. *Estrogen-like activity of perfluoroalkyl acids in vivo and interaction with human and rainbow trout estrogen receptors in vitro.* Toxicol Sci 120, 42-58.

Benninghoff, A.D., Orner, G.A., Buchner, C.H., Hendricks, J.D., Duffy, A.M., Williams, D.E., 2012. *Promotion of Hepatocarcinogenesis by Perfluoroalkyl Acids in Rainbow Trout.* Toxicol Sci 125, 69-78.

Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. *Assessing long-range transport potential of persistent organic pollutants.* Environ Sci Technol 34, 699-703.

Biegel, L.B., Hurtt, M.E., Frame, S.R., O'Connor, J.C., Cook, J.C., 2001. *Mechanisms of extrahepatic tumor induction by peroxisome proliferators in male CD rats*. Toxicol Sci 60, 44-55.

Biegel, L.B., Liu, R.C.M., Hurtt, M.E., Cook, J.C., 1995. *Effects of Ammonium Perfluorooctanoate on Leydig-Cell Function: In Vitro, in Vivo, and ex Vivo Studies.* Toxicol Appl Pharmacol 134, 18-25.

Bloom, M.S., Kannan, K., Spliethoff, H.M., Tao, L., Aldous, K.M., Vena, J.E., 2010. *Exploratory assessment of perfluorinated compounds and human thyroid function.* Physiology & behavior 99, 240-245.

Bonefeld-Jorgensen, E.C., Long, M., Bossi, R., Ayotte, P., Asmund, G., Kruger, T., Ghisari, M., Mulvad, G., Kern, P., Nzulumiki, P., Dewailly, E., 2011. *Perfluorinated compounds are related to breast cancer risk in Greenlandic Inuit: a case control study.* Environ Health 10, 88.

Bookstaff, R.C., Moore, R.W., Ingall, G.B., Peterson, R.E., 1990. *Androgenic deficiency in male rats treated with perfluorodecanoic acid.* Toxicol Appl Pharmacol 104, 322-333.

Brandsma, S.H., Smithwick, M., Solomon, K., Small, J., de Boer, J., Muir, D.C.G., 2011. *Dietary exposure of rainbow trout to 8:2 and 10:2 fluorotelomer alcohols and perfluorooctanesulfonamide: Uptake, transformation and elimination*. Chemosphere 82, 253-258.

Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. *Towards a global historical emission inventory for selected PCB congeners - A mass balance approach. 3. An update*. Science of the Total Environment 377, 296-307.

Breivik, K., Wania, F., Muir, D.C.G., Alaee, M., Backus, S., Pacepavicius, G., 2006. *Empirical and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether.* Environ Sci Technol 40, 4612-4618.

Brewster, D.W., Birnbaum, L.S., 1989. *The biochemical toxicity of perfluorodecanoic acid in the mouse is different from that of 2,3,7,8-tetrachlorodibenzo-p-dioxin*. Toxicol Appl Pharmacol 99, 544-554.

Butenhoff, J., Costa, G., Elcombe, C., Farrar, D., Hansen, K., Iwai, H., Jung, R., Kennedy, G., Jr., Lieder, P., Olsen, G., Thomford, P., 2002. *Toxicity of ammonium perfluorooctanoate in male cynomolgus monkeys after oral dosing for 6 months*. Toxicol Sci 69, 244-257.

Butenhoff, J.L., Bjork, J.A., Chang, S.C., Ehresman, D.J., Parker, G.A., Das, K., Lau, C., Lieder, P.H., van Otterdijk, F.M., Wallace, K.B., 2012. *Toxicological evaluation of ammonium perfluorobutyrate in rats: twenty-eight-day and ninety-day oral gavage studies*. Reprod Toxicol 33, 513-530.

Butenhoff, J.L., Chang, S.C., Ehresman, D.J., York, R.G., 2009. *Evaluation of potential reproductive and developmental toxicity of potassium perfluorohexanesulfonate in Sprague Dawley rats*. Reprod Toxicol 27, 331-341.

Butenhoff, J.L., Kennedy, G.L., Jr., Hinderliter, P.M., Lieder, P.H., Jung, R., Hansen, K.J., Gorman, G.S., Noker, P.E., Thomford, P.J., 2004. *Pharmacokinetics of perfluorooctanoate in cynomolgus monkeys.* Toxicol Sci 82, 394-406.

Chang, S.C., Das, K., Ehresman, D.J., Ellefson, M.E., Gorman, G.S., Hart, J.A., Noker, P.E., Tan, Y.M., Lieder, P.H., Lau, C., Olsen, G.W., Butenhoff, J.L., 2008. *Comparative pharmacokinetics of perfluorobutyrate in rats, mice, monkeys, and humans and relevance to human exposure via drinking water.* Toxicol Sci 104, 40-53.

Chen, M.H., Ha, E.H., Wen, T.W., Su, Y.N., Lien, G.W., Chen, C.Y., Chen, P.C., Hsieh, W.S., 2012. *Perfluorinated compounds in umbilical cord blood and adverse birth outcomes.* PLoS One 7, e42474.

Chengelis, C.P., Kirkpatrick, J.B., Radovsky, A., Shinohara, M., 2009. *A 90-day repeated dose oral (gavage) toxicity study of perfluorohexanoic acid (PFHxA) in rats (with functional observational battery and motor activity determinations).* Reprod Toxicol 27, 342-351.

Christensen, K.Y., Maisonet, M., Rubin, C., Holmes, A., Calafat, A.M., Kato, K., Flanders, W.D., Heron, J., McGeehin, M.A., Marcus, M., 2011. *Exposure to polyfluoroalkyl chemicals during pregnancy is not associated with offspring age at menarche in a contemporary British cohort.* Environ Int 37, 129-135.

Courrier, H.M., Krafft, M.P., Butz, N., Porté, C., Frossard, N., Rémy-Kristensen, A., Mély, Y., Pons, F., Vandamme, T.F., 2003. *Evaluation of cytotoxicity of new semi-fluorinated amphiphiles derived from dimorpholinophosphate.* Biomaterials 24, 689-696.

Corsini E, Sangivann E, Avogadro A, Galbati V, Viviani B, Marinovich M, Galli CL, Dell'Agli M, Germolec DR (2012) In vitro characterization of immunotoxic potential of several perfluornated compounds (PFCs), Toxicol Appl Pharmacol 258:248-255

D'Eon J, C., Mabury, S.A., 2011. *Exploring indirect sources of human exposure to perfluoroalkyl carboxylates (PFCAs): evaluating uptake, elimination, and biotransformation of polyfluoroalkyl phosphate esters (PAPs) in the rat*. Environ Health Perspect 119, 344-350.

D'Eon, J.C., Crozier, P.W., Furdui, V.I., Reiner, E.J., Libelo, E.L., Mabury, S.A., 2009. *Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers.* Environmental science & technology 43, 4589-4594.

D'Eon, J.C., Mabury, S.A., 2007. *Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): exploring routes of human contamination*. Environ Sci Technol 41, 4799-4805.

Dallaire, R., Dewailly, E., Pereg, D., Dery, S., Ayotte, P., 2009. *Thyroid function and plasma concentrations of polyhalogenated compounds in Inuit adults*. Environ Health Perspect 117, 1380-1386.

Das, K.P., Grey, B.E., Zehr, R.D., Wood, C.R., Butenhoff, J.L., Chang, S.C., Ehresman, D.J., Tan, Y.M., Lau, C., 2008. *Effects of perfluorobutyrate exposure during pregnancy in the mouse*. Toxicol Sci 105, 173-181.

Dinglasan-Panlilio, M.J.A., Mabury, S.A., 2006. *Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials.* Environmental Science & Technology 40, 1447-1453.

Dinglasan, M.J., Ye, Y., Edwards, E.A., Mabury, S.A., 2004. *Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids.* Environmental science & technology 38, 2857-2864.

DuPont, 2012. *Teflon - Uses and Applications*.

Ehresman, D.J., Froehlich, J.W., Olsen, G.W., Chang, S.C., Butenhoff, J.L., 2007. *Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals.* Environmental research 103, 176-184.

Emmett, E.A., Zhang, H., Shofer, F.S., Freeman, D., Rodway, N.V., Desai, C., Shaw, L.M., 2006. *Community exposure to perfluorooctanoate: relationships between serum levels and certain health parameters.* Journal of occupational and environmental medicine / American College of Occupational and Environmental Medicine 48, 771-779.

Eriksen, K.T., Raaschou-Nielsen, O., Sørensen, M., Roursgaard, M., Loft, S., Møller, P., 2010. *Genotoxic potential of the perfluorinated chemicals PFOA, PFOS, PFBS, PFNA and PFHxA in human HepG2 cells. Mutation Research.* Genetic Toxicology and Environmental Mutagenesis 700, 39-43.

Eriksen, K. T., M. Sørensen, J. K. McLaughlin, A. Tjønneland, K. Overvad and O. Raaschou-Nielsen (2010). "Determinants of Plasma PFOA and PFOS Levels Among 652 Danish Men." Environmental Science & Technology 45(19): 8137-8143.

Eriksen, K.T., Sorensen, M., McLaughlin, J.K., Lipworth, L., Tjonneland, A., Overvad, K., Raaschou-Nielsen, O., 2009. *Perfluorooctanoate and perfluorooctanesulfonate plasma levels and risk of cancer in the general Danish population*. J Natl Cancer Inst 101, 605-609.

Fang, X., Feng, Y., Wang, J., Dai, J., 2010. *Perfluorononanoic acid-induced apoptosis in rat spleen involves oxidative stress and the activation of caspase-independent death pathway*. Toxicology 267, 54-59.

Fang, X., Gao, G., Xue, H., Zhang, X., Wang, H., 2012. *Exposure of perfluorononanoic acid suppresses the hepatic insulin signal pathway and increases serum glucose in rats*. Toxicology 294, 109-115.

Fang, X., Zhang, L., Feng, Y., Zhao, Y., Dai, J., 2008. *Immunotoxic effects of perfluorononanoic acid on BALB/c mice.* Toxicol Sci 105, 312-321.

Fasano, W.J., Sweeney, L.M., Mawn, M.P., Nabb, D.L., Szostek, B., Buck, R.C., Gargas, M.L., 2009. *Kinetics of 8-2 fluorotelomer alcohol and its metabolites, and liver glutathione status following daily oral dosing for 45 days in male and female rats*. Chem Biol Interact 180, 281-295.

Fei, C., McLaughlin, J.K., Lipworth, L., Olsen, J., 2009. *Maternal levels of perfluorinated chemicals and subfecundity.* Hum Reprod 24, 1200-1205.

Fei, C., McLaughlin, J.K., Lipworth, L., Olsen, J., 2010. *Prenatal exposure to PFOA and PFOS and risk of hospitalization for infectious diseases in early childhood.* Environ Res 110, 773-777.

Fei, C., McLaughlin, J.K., Tarone, R.E., Olsen, J., 2007. *Perfluorinated chemicals and fetal growth: a study within the Danish National Birth Cohort.* Environ Health Perspect 115, 1677-1682.

Fei, C., McLaughlin, J.K., Tarone, R.E., Olsen, J., 2008. *Fetal growth indicators and perfluorinated chemicals: a study in the Danish National Birth Cohort.* Am J Epidemiol 168, 66-72.

Fei, C., Olsen, J., 2011. *Prenatal exposure to perfluorinated chemicals and behavioral or coordination problems at age 7 years.* Environ Health Perspect 119, 573-578.

Fernandez Freire, P., Perez Martin, J.M., Herrero, O., Peropadre, A., de la Pena, E., Hazen, M.J., 2008. *In vitro assessment of the cytotoxic and mutagenic potential of perfluorooctanoic acid.* Toxicol In Vitro 22, 1228-1233.

Fisher M, Arbuckle TE, Wade M, Haines DA (2013) Environ Res, doi: 10.1016/j.envres.2012.11.006

Fiedler, S., Pfister, G., Schramm, K.-W., 2010. *Poly- and perfluorinated compounds in household consumer products*. Toxicological & Environmental Chemistry 92, 1801-1811.

Fraser, A.J., Webster, T.F., Watkins, D.J., Nelson, J.W., Stapleton, H.M., Calafat, A.M., Kato, K., Shoeib, M., Vieira, V.M., McClean, M.D., 2012. *Polyfluorinated compounds in serum linked to indoor air in office environments*. Environmental science & technology 46, 1209-1215.

Freberg, B.I., Haug, L.S., Olsen, R., Daae, H.L., Hersson, M., Thomsen, C., Thorud, S., Becher, G., Molander, P., Ellingsen, D.G., 2010a. *Occupational exposure to airborne perfluorinated compounds during professional ski waxing.* Environ Sci Technol 44, 7723-7728.

Freberg, B.I., Haug, L.S., Olsen, R., Daae, H.L., Hersson, M., Thomsen, C., Thorud, S., Becher, G., Molander, P., Ellingsen, D.G., 2010b. *Occupational exposure to airborne perfluorinated compounds during professional ski waxing.* Environ Sci Technol 44, 7723-7728.

Frisbee, S.J., Shankar, A., Knox, S.S., Steenland, K., Savitz, D.A., Fletcher, T., Ducatman, A.M., 2010. *Perfluorooctanoic acid, perfluorooctanesulfonate, and serum lipids in children and adolescents: results from the C8 Health Project.* Arch Pediatr Adolesc Med 164, 860-869.

Fromme, H., Tittlemier, S.A., Völkel, W., Wilhelm, M., Twardella, D., 2009. *Perfluorinated compounds – Exposure assessment for the general population in western countries*. Int J Hyg Environ Health 212, 239-270.

Gallo, V., Leonardi, G., Genser, B., Lopez-Espinosa, M.J., Frisbee, S.J., Karlsson, L., Ducatman, A.M., Fletcher, T., 2012. *Serum perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) concentrations and liver function biomarkers in a population with elevated PFOA exposure.* Environ Health Perspect 120, 655-660.

Gewurtz, S.B., Bhavsar, S.P., Crozier, P.W., Diamond, M.L., Helm, P.A., Marvin, C.H., Reiner, E.J., 2009. *Perfluoroalkyl contaminants in window film: indoor/outdoor, urban/rural, and winter/summer contamination and assessment of carpet as a possible source.* Environ Sci Technol 43, 7317-7323.

Gilliland, F.D., Mandel, J.S., 1993. *Mortality among employees of a perfluorooctanoic acid production plant*. Journal of occupational medicine : official publication of the Industrial Medical Association 35, 950-954.

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.

Goorha, Y.K., Deb, P., Chatterjee, T., Dhot, P.S., Prasad, R.S., 2003. *Artifical blood.* Medical Journal Armed Forces India 59, 45-50.

Grandjean, P., Andersen, E.W., Budtz-Jorgensen, E., Nielsen, F., Molbak, K., Weihe, P., Heilmann, C., 2012. *Serum vaccine antibody concentrations in children exposed to perfluorinated compounds.* JAMA 307, 391-397.

Granum B, Haug LS, Namork E, Stolevik SB, Thomsen C, Aaberge IS, van Loveren H, Lovik M, Nygaard UC (2013) Pre-natal exposure to perfluoroalkyl substances may be associated with altered vaccine antibody levels and immune-related health outcomes in early childhood, J Immunotoxicol DOI: 10.3109/1547691X.2012.755580

Grice, M.M., Alexander, B.H., Hoffbeck, R., Kampa, D.M., 2007. *Self-reported medical conditions in perfluorooctanesulfonyl fluoride manufacturing workers*. Journal of occupational and environmental medicine / American College of Occupational and Environmental Medicine 49, 722-729.

Gump, B.B., Wu, Q., Dumas, A.K., Kannan, K., 2011. *Perfluorochemical (PFC) exposure in children: associations with impaired response inhibition.* Environ Sci Technol 45, 8151-8159.

Gutzkow, K.B., Haug, L.S., Thomsen, C., Sabaredzovic, A., Becher, G., Brunborg, G., 2012. *Placental transfer of perfluorinated compounds is selective--a Norwegian Mother and Child sub-cohort study*. Int J Hyg Environ Health 215, 216-219.

Hagenaars, A., Meyer, I.J., Herzke, D., Pardo, B.G., Martinez, P., Pabon, M., De Coen, W., Knapen, D., 2011. *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 104, 168-176.

Hagenaars A, Vergauwen L, De Coen W, Knapen D (2011) Structure-activity relationship assessment of four perfluorinated chemicals using a prolonged zebrafish early life stage test, Chemosphere 82:764-772

Halldorsson, T.I., Fei, C., Olsen, J., Lipworth, L., McLaughlin, J.K., Olsen, S.F., 2008. *Dietary predictors of perfluorinated chemicals: a study from the Danish National Birth Cohort.* Environ Sci Technol 42, 8971-8977.

Halldorsson, T.I., Rytter, D., Haug, L.S., Bech, B.H., Danielsen, I., Becher, G., Henriksen, T.B., Olsen, S.F., 2012. *Prenatal exposure to perfluorooctanoate and risk of overweight at 20 years of age: a prospective cohort study.* Environ Health Perspect 120, 668-673.

Hamm, M.P., Cherry, N.M., Chan, E., Martin, J.W., Burstyn, I., 2010. *Maternal exposure to perfluorinated acids and fetal growth.* J Expo Sci Environ Epidemiol 20, 589-597.

Harris, M.W., Birnbaum, L.S., 1989. *Developmental toxicity of perfluorodecanoic acid in C57BL/6N mice.* Fundamental and applied toxicology : official journal of the Society of Toxicology 12, 442-448.

Harris, M.W., Uraih, L.C., Birnbaum, L.S., 1989. *Acute toxicity of perfluorodecanoic acid in C57BL/6 mice differs from 2,3,7,8-tetrachlorodibenzo-p-dioxin.* Fundamental and applied toxicology : official journal of the Society of Toxicology 13, 723-736.

Haug, L.S., Huber, S., Becher, G., Thomsen, C., 2011. *Characterisation of human exposure pathways to perfluorinated compounds--comparing exposure estimates with biomarkers of exposure.* Environ Int 37, 687-693.

Haug, L.S., Thomsen, C., Becher, G., 2009. *Time trends and the influence of age and gender on serum concentrations of perfluorinated compounds in archived human samples.* Environ Sci Technol 43, 2131-2136.

Herzke, D., Olsson, E., Posner, S., 2012. *Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway - a pilot study*. Chemosphere 88, 980-987.

Hinderliter, P.M., Mylchreest, E., Gannon, S.A., Butenhoff, J.L., Kennedy, G.L., Jr., 2005. *Perfluorooctanoate: Placental and lactational transport pharmacokinetics in rats*. Toxicology 211, 139-148.

Hoang, K.C., Edris, A., Su, J., Mukai, D.S., Mahon, S., Petrov, A.D., Kern, M., Ashan, C., Chen, Z., Tromberg, B.J., Narula, J., Brenner, M., 2009. *Use of an oxygen-carrying blood substitute to improve intravascular optical coherence tomography imaging*. Journal of biomedical optics 14, 034028.

Hoffman, K., Webster, T.F., Weisskopf, M.G., Weinberg, J., Vieira, V.M., 2010. *Exposure to polyfluoroalkyl chemicals and attention deficit/hyperactivity disorder in U.S. children 12-15 years of age*. Environ Health Perspect 118, 1762-1767.

Hoke, R.A., Bouchelle, L.D., Ferrell, B.D., Buck, R.C., 2012. *Comparative acute freshwater hazard assessment and preliminary PNEC development for eight fluorinated acids*. Chemosphere 87, 725-733.

Hu, W., Jones, P.D., Upham, B.L., Trosko, J.E., Lau, C., Giesy, J.P., 2002. *Inhibition of Gap Junctional Intercellular Communication by Perfluorinated Compounds in Rat Liver and Dolphin Kidney Epithelial Cell Lines in Vitro and Sprague-Dawley Rats in Vivo.* Toxicol Sci 68, 429-436.

Huber, S., Haug, L.S., Schlabach, M., 2011. *Per- and polyfluorinated compounds in house dust and indoor air from northern Norway – A pilot study.* Chemosphere 84, 1686-1693.

Inoue, K., Okada, F., Ito, R., Kato, S., Sasaki, S., Nakajima, S., Uno, A., Saijo, Y., Sata, F., Yoshimura, Y., Kishi, R., Nakazawa, H., 2004. *Perfluorooctane sulfonate (PFOS) and related perfluorinated compounds in human maternal and cord blood samples: assessment of PFOS exposure in a susceptible population during pregnancy.* Environ Health Perspect 112, 1204-1207.

Intrasuksri, U., Feller, D.R., 1991. *Comparison of the effects of selected monocarboxylic, dicarboxylic and perfluorinated fatty acids on peroxisome proliferation in primary cultured rat hepatocytes.* Biochem Pharmacol 42, 184-188.

Intrasuksri, U., Rangwala, S.M., O'Brien, M., Noonan, D.J., Feller, D.R., 1998. *Mechanisms of peroxisome proliferation by perfluorooctanoic acid and endogenous fatty acids.* General pharmacology 31, 187-197.

Ishibashi, H., Ishida, H., Matsuoka, M., Tominaga, N., Arizono, K., 2007. *Estrogenic Effects of Fluorotelomer Alcohols for Human Estrogen Receptor Isoforms alpha and beta in Vitro.* Biological and Pharmaceutical Bulletin 30, 1358-1359.

Ishibashi, H., Yamauchi, R., Matsuoka, M., Kim, J.-W., Hirano, M., Yamaguchi, A., Tominaga, N., Arizono, K., 2008a. *Fluorotelomer alcohols induce hepatic vitellogenin through activation of the estrogen receptor in male medaka (Oryzias latipes)*. Chemosphere 71, 1853-1859.

Ishibashi, H., Yamauchi, R., Matsuoka, M., Kim, J.W., Hirano, M., Yamaguchi, A., Tominaga, N., Arizono, K., 2008b. *Fluorotelomer alcohols induce hepatic vitellogenin through activation of the estrogen receptor in male medaka (Oryzias latipes).* Chemosphere 71, 1853-1859.

Jensen, M.S., Norgaard-Pedersen, B., Toft, G., Hougaard, D.M., Bonde, J.P., Cohen, A., Thulstrup, A.M., Ivell, R., Anand-Ivell, R., Lindh, C.H., Jonsson, B.A., 2012. *Phthalates and perfluorooctanesulfonic acid in human amniotic fluid: temporal trends and timing of amniocentesis in pregnancy.* Environ Health Perspect 120, 897-903.

Jensen, M. S., B. Norgaard-Pedersen, G. Toft, D. M. Hougaard, J. P. Bonde, A. Cohen, A. M. Thulstrup, R. Ivell, R. Anand-Ivell, C. H. Lindh and B. A. Jonsson (2012). "Phthalates and perfluorooctanesulfonic acid in human amniotic fluid: temporal trends and timing of amniocentesis in pregnancy." Environ Health Perspect 120(6): 897-903.

Ji, K., Kim, S., Kho, Y., Paek, D., Sakong, J., Ha, J., Choi, K., 2012. *Serum concentrations of major perfluorinated compounds among the general population in Korea: dietary sources and potential impact on thyroid hormones.* Environ Int 45, 78-85.

Joensen, U.N., Bossi, R., Leffers, H., Jensen, A.A., Skakkebaek, N.E., Jorgensen, N., 2009. *Do perfluoroalkyl compounds impair human semen quality?* Environ Health Perspect 117, 923-927.

Johansson, N., Fredriksson, A., Eriksson, P., 2008. *Neonatal exposure to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) causes neurobehavioural defects in adult mice*. Neurotoxicology 29, 160-169.

Jones, P.D., Hu, W., De Coen, W., Newsted, J.L., Giesy, J.P., 2003. *Binding of perfluorinated fatty acids to serum proteins.* Environ Toxicol Chem 22, 2639-2649.

Karrman, A., Ericson, I., van Bavel, B., Darnerud, P.O., Aune, M., Glynn, A., Lignell, S., Lindstrom, G., 2007a. *Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996-2004, in Sweden.* Environ Health Perspect 115, 226-230.

Karrman, A., Langlois, I., van Bavel, B., Lindstrom, G., Oehme, M., 2007b. *Identification and pattern of perfluorooctane sulfonate (PFOS) isomers in human serum and plasma*. Environ Int 33, 782-788.

Karrman, A., van Bavel, B., Jarnberg, U., Hardell, L., Lindstrom, G., 2006. *Perfluorinated chemicals in relation to other persistent organic pollutants in human blood.* Chemosphere 64, 1582-1591.

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.

Kawashima, Y., Kobayashi, H., Miura, H., Kozuka, H., 1995. *Characterization of hepatic responses of rat to administration of perfluorooctanoic and perfluorodecanoic acids at low levels*. Toxicology 99, 169-178.

Kennedy, G.L., Jr., Butenhoff, J.L., Olsen, G.W., O'Connor, J.C., Seacat, A.M., Perkins, R.G., Biegel, L.B., Murphy, S.R., Farrar, D.G., 2004. *The toxicology of perfluorooctanoate.* Crit Rev Toxicol 34, 351-384.

Kim, S., Choi, K., Ji, K., Seo, J., Kho, Y., Park, J., Park, S., Hwang, I., Jeon, J., Yang, H., Giesy, J.P., 2011. *Trans-placental transfer of thirteen perfluorinated compounds and relations with fetal thyroid hormones.* Environ Sci Technol 45, 7465-7472.

Kleszczyński, K., Gardzielewski, P., Mulkiewicz, E., Stepnowski, P., Składanowski, A.C., 2007. *Analysis of structure–cytotoxicity in vitro relationship (SAR) for perfluorinated carboxylic acids*. Toxicology in Vitro 21, 1206-1211.

Kleszczyński, K., Składanowski, A.C., 2009. Mechanism of cytotoxic action of perfluorinated acids.: I. *Alteration in plasma membrane potential and intracellular pH level.* Toxicology and Applied Pharmacology 234, 300-305.

Knox, S.S., Jackson, T., Frisbee, S.J., Javins, B., Ducatman, A.M., 2011a. *Perfluorocarbon exposure, gender and thyroid function in the C8 Health Project*. J Toxicol Sci 36, 403-410.

Knox, S.S., Jackson, T., Javins, B., Frisbee, S.J., Shankar, A., Ducatman, A.M., 2011b. *Implications of early menopause in women exposed to perfluorocarbons*. J Clin Endocrinol Metab 96, 1747-1753.

Kudo, N., Iwase, Y., Okayachi, H., Yamakawa, Y., Kawashima, Y., 2005. *Induction of hepatic peroxisome proliferation by 8-2 telomer alcohol feeding in mice: formation of perfluorooctanoic acid in the liver*. Toxicol Sci 86, 231-238.

Ladics, G.S., Kennedy, G.L., O'Connor, J., Everds, N., Malley, L.A., Frame, S.R., Gannon, S., Jung, R., Roth, T., Iwai, H., Shin-Ya, S., 2008. *90-day oral gavage toxicity study of 8-2 fluorotelomer alcohol in rats.* Drug Chem Toxicol 31, 189-216.

Latała, A., Nędzi, M., Stepnowski, P., 2009. *Acute toxicity assessment of perfluorinated carboxylic acids towards the Baltic microalgae.* Environmental Toxicology and Pharmacology 28, 167-171.

Lau, C., 2012. *Perfluoroalkyl acids: Recent research highlights.* Reprod Toxicol 33, 405-409.

Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. *Perfluoroalkyl acids: a review of monitoring and toxicological findings.* Toxicol Sci 99, 366-394.

Lau, C., Butenhoff, J.L., Rogers, J.M., 2004. *The developmental toxicity of perfluoroalkyl acids and their derivatives.* Toxicol Appl Pharmacol 198, 231-241.

Lau, C., Thibodeaux, J.R., Hanson, R.G., Narotsky, M.G., Rogers, J.M., Lindstrom, A.B., Strynar, M.J., 2006. *Effects of perfluorooctanoic acid exposure during pregnancy in the mouse*. Toxicol Sci 90, 510-518.

Lau, C., Thibodeaux, J.R., Hanson, R.G., Rogers, J.M., Grey, B.E., Stanton, M.E., Butenhoff, J.L., Stevenson, L.A., 2003. *Exposure to perfluorooctane sulfonate during pregnancy in rat and mouse. II: postnatal evaluation.* Toxicol Sci 74, 382-392.

Lee, H., Mabury, S.A., 2011. *A pilot survey of legacy and current commercial fluorinated chemicals in human sera from United States donors in 2009.* Environmental science & technology 45, 8067-8074.

Lehmler, H.-J., 2005. *Synthesis of environmentally relevant fluorinated surfactants—a review*. Chemosphere 58, 1471-1496.

Lieder, P.H., Chang, S.C., York, R.G., Butenhoff, J.L., 2009a. *Toxicological evaluation of potassium perfluorobutanesulfonate in a 90-day oral gavage study with Sprague-Dawley rats*. Toxicology 255, 45-52.

Lieder, P.H., York, R.G., Hakes, D.C., Chang, S.C., Butenhoff, J.L., 2009b. *A two-generation oral gavage reproduction study with potassium perfluorobutanesulfonate (K+PFBS) in Sprague Dawley rats.* Toxicology 259, 33-45.

Lin, C.Y., Chen, P.C., Lin, Y.C., Lin, L.Y., 2009. *Association among serum perfluoroalkyl chemicals, glucose homeostasis, and metabolic syndrome in adolescents and adults.* Diabetes care 32, 702-707.

Lindeman, B., Maass, C., Duale, N., Gutzkow, K.B., Brunborg, G., Andreassen, A., 2012a. *Effects of per- and polyfluorinated compounds on adult rat testicular cells following in vitro exposure.* Reprod Toxicol 33, 531-537.

Lindeman, B., Maass, C., Duale, N., Gützkow, K.B., Brunborg, G., Andreassen, Å., 2012b. *Effects of per- and polyfluorinated compounds on adult rat testicular cells following in vitro exposure.* Reproductive Toxicology 33, 531-537.

Lindh, C.H., Rylander, L., Toft, G., Axmon, A., Rignell-Hydbom, A., Giwercman, A., Pedersen, H.S., Goalczyk, K., Ludwicki, J.K., Zvyezday, V., Vermeulen, R., Lenters, V., Heederik, D., Bonde, J.P., Jonsson, B.A., 2012. *Blood serum concentrations of perfluorinated compounds in men from Greenlandic Inuit and European populations.* Chemosphere 88, 1269-1275.

Liu, C., Deng, J., Yu, L., Ramesh, M., Zhou, B., 2010a. *Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alcohol.* Aquat Toxicol 96, 70-76.

Liu, C., Deng, J., Yu, L., Ramesh, M., Zhou, B., 2010b. *Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alcohol.* Aquatic Toxicology 96, 70-76.

Liu, C., Yu, L., Deng, J., Lam, P.K.S., Wu, R.S.S., Zhou, B., 2009. *Waterborne exposure to fluorotelomer alcohol 6:2 FTOH alters plasma sex hormone and gene transcription in the hypothalamic–pituitary–gonadal (HPG) axis of zebrafish.* Aquatic Toxicology 93, 131-137.

Liu, C., Zhang, X., Chang, H., Jones, P., Wiseman, S., Naile, J., Hecker, M., Giesy, J.P., Zhou, B., 2010c. *Effects of fluorotelomer alcohol 8:2 FTOH on steroidogenesis in H295R cells: targeting the cAMP signalling cascade.* Toxicol Appl Pharmacol 247, 222-228.

Liu, C., Zhang, X., Chang, H., Jones, P., Wiseman, S., Naile, J., Hecker, M., Giesy, J.P., Zhou, B., 2010d. *Effects of fluorotelomer alcohol 8:2 FTOH on steroidogenesis in H295R cells: Targeting the cAMP signalling cascade.* Toxicology and Applied Pharmacology 247, 222-228.

Liu, J., J. Li, Y. Liu, H. M. Chan, Y. Zhao, Z. Cai and Y. Wu (2011). "Comparison on gestation and lactation exposure of perfluorinated compounds for newborns." Environment International 37(7): 1206-1212.

Long, M., Bossi, R., Bonefeld-Jorgensen, E.C., 2012. *Level and temporal trend of perfluoroalkyl acids in Greenlandic Inuit*. Int J Circumpolar Health 71, 17998.

Lopez-Espinosa, M.J., Mondal, D., Armstrong, B., Bloom, M.S., Fletcher, T., 2012. *Thyroid function and perfluoroalkyl acids in children living near a chemical plant*. Environ Health Perspect 120, 1036-1041.

Loveless, S.E., Slezak, B., Serex, T., Lewis, J., Mukerji, P., O'Connor, J.C., Donner, E.M., Frame, S.R., Korzeniowski, S.H., Buck, R.C., 2009. *Toxicological evaluation of sodium perfluorohexanoate*. Toxicology 264, 32-44.

Luebker, D.J., Case, M.T., York, R.G., Moore, J.A., Hansen, K.J., Butenhoff, J.L., 2005a. *Two-generation reproduction and cross-foster studies of perfluorooctanesulfonate (PFOS) in rats*. Toxicology 215, 126-148.

Luebker, D.J., York, R.G., Hansen, K.J., Moore, J.A., Butenhoff, J.L., 2005b. *Neonatal mortality from in utero exposure to perfluorooctanesulfonate (PFOS) in Sprague-Dawley rats: dose-response, and biochemical and pharamacokinetic parameters*. Toxicology 215, 149-169.

Lundin, J.I., Alexander, B.H., Olsen, G.W., Church, T.R., 2009. *Ammonium perfluorooctanoate production and occupational mortality.* Epidemiology 20, 921-928.

MacNeil, J., Steenland, N.K., Shankar, A., Ducatman, A., 2009. *A cross-sectional analysis of type II diabetes in a community with exposure to perfluorooctanoic acid (PFOA).* Environ Res 109, 997-1003.

Maisonet, M., Terrell, M.L., McGeehin, M.A., Christensen, K.Y., Holmes, A., Calafat, A.M., Marcus, M., 2012. *Maternal Concentrations of Polyfluoroalkyl Compounds during Pregnancy and Fetal and Postnatal Growth in British Girls.* Environ Health Perspect 120, 1432-1437.

Malinverno, G., Pantini, G., Bootman, J., 1996. *Safety evaluation of perfluoropolyethers, liquid polymers used in barrier creams and other skin-care products.* Food Chem Toxicol 34, 639-650.

Maras, M., Vanparys, C., Muylle, F., Robbens, J., Berger, U., Barber, J.L., Blust, R., De Coen, W., 2006. *Estrogen-like properties of fluorotelomer alcohols as revealed by mcf-7 breast cancer cell proliferation*. Environ Health Perspect 114, 100-105.

Mariussen, E., 2012. *Neurotoxic effects of perfluoroalkylated compounds: mechanisms of action and environmental relevance*. Archives of toxicology 86, 1349-1367.

Martin, J.W., Mabury, S.A., O'Brien, P.J., 2005. *Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes.* Chemico-Biological Interactions 155, 165-180.

Melzer, D., Rice, N., Depledge, M.H., Henley, W.E., Galloway, T.S., 2010. *Association between serum perfluorooctanoic acid (PFOA) and thyroid disease in the U.S. National Health and Nutrition Examination Survey.* Environ Health Perspect 118, 686-692.

Mertens, J.J., Sved, D.W., Marit, G.B., Myers, N.R., Stetson, P.L., Murphy, S.R., Schmit, B., Shinohara, M., Farr, C.H., 2010. *Subchronic toxicity of S-111-S-WB in Sprague Dawley rats*. Int J Toxicol 29, 358-371.

Mitchell, R.J., Myers, A.L., Mabury, S.A., Solomon, K.R., Sibley, P.K., 2011. *Toxicity of fluorotelomer carboxylic acids to the algae Pseudokirchneriella subcapitata and Chlorella vulgaris, and the amphipod Hyalella azteca*. Ecotoxicology and Environmental Safety 74, 2260-2267.

Moe, M.K., Huber, S., Svenson, J., Hagenaars, A., Pabon, M., Trümper, M., Berger, U., Knapen, D., Herzke, D., 2012. *The structure of the fire fighting foam surfactant Forafac®1157 and its biological and photolytic transformation products*. Chemosphere 89, 869-875.

Monroy, R., Morrison, K., Teo, K., Atkinson, S., Kubwabo, C., Stewart, B., Foster, W.G., 2008. *Serum levels of perfluoroalkyl compounds in human maternal and umbilical cord blood samples*. Environ Res 108, 56-62.

Mulkiewicz, E., Jastorff, B., Składanowski, A.C., Kleszczyński, K., Stepnowski, P., 2007. *Evaluation of the acute toxicity of perfluorinated carboxylic acids using eukaryotic cell lines, bacteria and enzymatic assays.* Environmental Toxicology and Pharmacology 23, 279-285.

Mundt, D.J., Mundt, K.A., Luippold, R.S., Schmidt, M.D., Farr, C.H., 2007. *Clinical epidemiological study of employees exposed to surfactant blend containing perfluorononanoic acid.* Occup Environ Med 64, 589-594.

Mylchreest, E., Ladics, G.S., Munley, S.M., Buck, R.C., Stadler, J.C., 2005a. *Evaluation of the reproductive and developmental toxicity of a fluoroalkylethanol mixture.* Drug Chem Toxicol 28, 159-175.

Mylchreest, E., Munley, S.M., Kennedy, G.L., Jr., 2005b. *Evaluation of the developmental toxicity of 8-2 telomer B alcohol.* Drug Chem Toxicol 28, 315-328.

Naile J, Wiseman S, Bachtold K, Jones PD, Giesy JP (2012) Transcriptional effects of perfluorinated compounds in rat hepatoma cells, Chemosphere 86:270-277

Needham, L.L., Grandjean, P., Heinzow, B., Jørgensen, P.J., Nielsen, F., Patterson, D.G., Sjödin, A., Turner, W.E., Weihe, P., 2010. *Partition of Environmental Chemicals between Maternal and Fetal Blood and Tissues.* Environ Sci Technol 45, 1121-1126.

Newsted JL, Beach SA, Gallagher SP, Giesy JP. 2008. Acute and chronic effects of perfluorobutane sulfonate (PFBS) on the Mallard and Northern Bobwhite quail. Archives of Environmental Contamination and Toxicology 54: 535–545.

Nelson, J.W., Hatch, E.E., Webster, T.F., 2010. *Exposure to polyfluoroalkyl chemicals and cholesterol, body weight, and insulin resistance in the general U.S. population*. Environ Health Perspect 118, 197-202.

Nilsson, H., Karrman, A., Rotander, A., van Bavel, B., Lindstrom, G., Westberg, H., 2010a. *Inhalation exposure to fluorotelomer alcohols yield perfluorocarboxylates in human blood?* Environ Sci Technol 44, 7717-7722.

Nilsson, H., Karrman, A., Westberg, H., Rotander, A., van Bavel, B., Lindstrom, G., 2010b. *A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax.* Environ Sci Technol 44, 2150-2155.

Nilsson, S., Makela, S., Treuter, E., Tujague, M., Thomsen, J., Andersson, G., Enmark, E., Pettersson, K., Warner, M., Gustafsson, J.A., 2001. *Mechanisms of estrogen action*. Physiol Rev 81, 1535-1565.

Nobels, I., Dardenne, F., Coen, W.D., Blust, R., 2010. *Application of a multiple endpoint bacterial reporter assay to evaluate toxicological relevant endpoints of perfluorinated compounds with different functional groups and varying chain length.* Toxicology in Vitro 24, 1768-1774.

O'Brien, J.M., Crump, D., Mundy, L.J., Chu, S., McLaren, K.K., Vongphachan, V., Letcher, R.J., Kennedy, S.W., 2009. *Pipping success and liver mRNA expression in chicken embryos exposed in ovo to C8 and C11 perfluorinated carboxylic acids and C10 perfluorinated sulfonate.* Toxicology Letters 190, 134-139.

Oda, Y., Nakayama, S., Harada, K., Koizumi, A., 2007. *Negative results of umu genotoxicity test of fluorotelomer alcohols and perfluorinated alkyl acids.* Environmental Health and Preventive Medicine 12, 217-219.

Okada, E., Sasaki, S., Saijo, Y., Washino, N., Miyashita, C., Kobayashi, S., Konishi, K., Ito, Y.M., Ito, R., Nakata, A., Iwasaki, Y., Saito, K., Nakazawa, H., Kishi, R., 2012. *Prenatal exposure to perfluorinated chemicals and relationship with allergies and infectious diseases in infants.* Environ Res 112, 118-125.

Oldham ED, Xie W, Farnoud AM, Fiegel J, Lehmler HJ (2012) Disruption of phosphatidylcholine monolayers and bilayers by perfluorobutane sulphonate, J Phys Chem B 116:9999-10007

Olsen, G.W., Burris, J.M., Mandel, J.H., Zobel, L.R., 1999. *Serum perfluorooctane sulfonate and hepatic and lipid clinical chemistry tests in fluorochemical production employees.* Journal of occupational and environmental medicine / American College of Occupational and Environmental Medicine 41, 799-806.

Olsen, G.W., Chang, S.C., Noker, P.E., Gorman, G.S., Ehresman, D.J., Lieder, P.H., Butenhoff, J.L., 2009. *A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans.* Toxicology 256, 65-74.

Olsen, G.W., Gilliland, F.D., Burlew, M.M., Burris, J.M., Mandel, J.S., Mandel, J.H., 1998. *An epidemiologic investigation of reproductive hormones in men with occupational exposure to perfluorooctanoic acid.* Journal of occupational and environmental medicine / American College of Occupational and Environmental Medicine 40, 614-622.

Olsen, G.W., Zobel, L.R., 2007. *Assessment of lipid, hepatic, and thyroid parameters with serum perfluorooctanoate (PFOA) concentrations in fluorochemical production workers.* International archives of occupational and environmental health 81, 231-246.

Permadi, H., Lundgren, B., Andersson, K., DePierre, J.W., 1992. *Effects of perfluoro fatty acids on xenobiotic-metabolizing enzymes, enzymes which detoxify reactive forms of oxygen and lipid peroxidation in mouse liver.* Biochem Pharmacol 44, 1183-1191.

Pinkas, A., Slotkin, T.A., Brick-Turin, Y., Van der Zee, E.A., Yanai, J., 2010. *Neurobehavioral teratogenicity of perfluorinated alkyls in an avian model*. Neurotoxicol Teratol 32, 182-186.

Pistocchi, A., Loos, R., 2009. *A map of European emissions and concentrations of PFOS and PFOA*. Environmental Science and Technology 43, 9237-9244.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. *Sources, fate and transport of perfluorocarboxylates*. Environ Sci Technol 40, 32-44.

Porpora MG, Lucchini R, Abballe A, Ingelido AM, Valentini S, Fuggetta E, Cardi V, Ticino A, Marra V, Fulgenzi AR, Felip ED (2013) Placental transfer of persistent organic pollutants: a preliminary study on mother-newborn pairs, Int J Environ Res Public Health 10:699-711

Rand, A.A., Mabury, S.A., 2012a. *Assessing the structure-activity relationships of fluorotelomer unsaturated acids and aldehydes with glutathione Reactivity of glutathione with fluorotelomer unsaturated acids and aldehydes.* Cell Biol Toxicol 28, 115-124.

Rand, A.A., Mabury, S.A., 2012b. *Assessing the structure-activity relationships of fluorotelomer unsaturated acids and aldehydes with glutathione. Reactivity of glutathione with fluorotelomer unsaturated acids and aldehydes*. Cell Biol Toxicol 28, 115-124.

Raymer, J.H., Michael, L.C., Studabaker, W.B., Olsen, G.W., Sloan, C.S., Wilcosky, T., Walmer, D.K., 2012. *Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) and their associations with human semen quality measurements.* Reprod Toxicol 33, 419-427.

Riess, J.G., 2002. *Blood substitutes and other potential biomedical applications of fluorinated colloids.* Journal of Fluorine Chemistry 114, 119-126.

Riess, J.G., Krafft, M.P., 1998. *Fluorinated materials for in vivo oxygen transport (blood substitutes), diagnosis and drug delivery*. Biomaterials 19, 1529-1539.

Rosenmai, A.K., Nielsen, F.K., Pedersen, M., Hadrup, N., Trier, X., Christensen, J.H., Vinggaard, A.M., 2012. *Fluorochemicals used in food packaging inhibit male sex hormone synthesis.* Toxicol Appl Pharmacol.

Rylander, C., Brustad, M., Falk, H., Sandanger, T.M., 2009. *Dietary predictors and plasma concentrations of perfluorinated compounds in a coastal population from northern Norway.* J Environ Public Health 2009, 268219.

Sakr, C.J., Leonard, R.C., Kreckmann, K.H., Slade, M.D., Cullen, M.R., 2007. *Longitudinal study of serum lipids and liver enzymes in workers with occupational exposure to ammonium perfluorooctanoate.* Journal of occupational and environmental medicine / American College of Occupational and Environmental Medicine 49, 872-879.

Savitz, D.A., Stein, C.R., Elston, B., Wellenius, G.A., Bartell, S.M., Shin, H.M., Vieira, V.M., Fletcher, T., 2012. *Relationship of perfluorooctanoic Acid exposure to pregnancy outcome based on birth records in the mid-ohio valley*. Environ Health Perspect 120, 1201-1207.

Shankar, A., Xiao, J., Ducatman, A., 2012. *Perfluorooctanoic Acid and Cardiovascular Disease in US Adults*. Arch Intern Med, 1-7.

Shi, Z., Ding, L., Zhang, H., Feng, Y., Xu, M., Dai, J., 2009. *Chronic exposure to perfluorododecanoic acid disrupts testicular steroidogenesis and the expression of related genes in male rats.* Toxicol Lett 188, 192-200.

Shi, Z., Zhang, H., Liu, Y., Xu, M., Dai, J., 2007. *Alterations in gene expression and testosterone synthesis in the testes of male rats exposed to perfluorododecanoic acid.* Toxicol Sci 98, 206-215.

Sibinski, L.J., 1987. *Final report of a two year oral (diet) toxicity and carcinogenicity study of fluorochemical FC-143 (perfluorooctanane ammonium carboxylate) in rats*. 3M Company/RIKER Exp No 0281CR0012; 8EHQ-1087-0394 1–4.

Sinclair, E., Kim, S.K., Akinleye, H.B., Kannan, K., 2007. *Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags*. Environ Sci Technol 41, 1180-1185.

Slotkin TA, MacKillopEA, Melnick RL, Thayer KA, Seidler FJ (2008) Developmental neurotoxicity of perfluorinated chemicals modeled in vitro, Environ Health Perspect 116:716-722

So, M.K., Yamashita, N., Taniyasu, S., Jiang, Q., Giesy, J.P., Chen, K., Lam, P.K., 2006. *Health risks in infants associated with exposure to perfluorinated compounds in human breast milk from Zhoushan, China*. Environ Sci Technol 40, 2924-2929.

Steenland, K., Fletcher, T., Savitz, D.A., 2010a. *Epidemiologic evidence on the health effects of perfluorooctanoic acid (PFOA).* Environ Health Perspect 118, 1100-1108.

Steenland, K., Tinker, S., Frisbee, S., Ducatman, A., Vaccarino, V., 2009. *Association of perfluorooctanoic acid and perfluorooctane sulfonate with serum lipids among adults living near a chemical plant*. Am J Epidemiol 170, 1268-1278.

Steenland, K., Tinker, S., Shankar, A., Ducatman, A., 2010b. *Association of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) with uric acid among adults with elevated community exposure to PFOA.* Environ Health Perspect 118, 229-233.

Stein, C.R., Savitz, D.A., 2011. *Serum perfluorinated compound concentration and attention deficit/hyperactivity disorder in children 5-18 years of age.* Environ Health Perspect 119, 1466-1471.

Stein, C.R., Wolff, M.S., Calafat, A.M., Kato, K., Engel, S.M., 2012. *Comparison of polyfluoroalkyl compound concentrations in maternal serum and amniotic fluid: A pilot study*. Reprod Toxicol 34, 312-316.

Sundstrom, M., D. J. Ehresman, A. Bignert, J. L. Butenhoff, G. W. Olsen, S. C. Chang and A. Bergman (2011). "A temporal trend study (1972-2008) of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in pooled human milk samples from Stockholm, Sweden." Environ Int 37(1): 178-183.

Takagi, A., Sai, K., Umemura, T., Hasegawa, R., Kurokawa, Y., 1991. *Short-term exposure to the peroxisome proliferators, perfluorooctanoic acid and perfluorodecanoic acid, causes significant increase of 8-hydroxydeoxyguanosine in liver DNA of rats.* Cancer Lett 57, 55-60.

Takagi, A., Sai, K., Umemura, T., Hasegawa, R., Kurokawa, Y., 1992. *Hepatomegaly is an early biomarker for hepatocarcinogenesis induced by peroxisome proliferators.* J Environ Pathol Toxicol Oncol 11, 145-149.

Thibodeaux, J.R., Hanson, R.G., Rogers, J.M., Grey, B.E., Barbee, B.D., Richards, J.H., Butenhoff, J.L., Stevenson, L.A., Lau, C., 2003. *Exposure to perfluorooctane sulfonate during pregnancy in rat and mouse. I: maternal and prenatal evaluations.* Toxicol Sci 74, 369-381.

Thomsen, C., L. S. Haug, H. Stigum, M. Froshaug, S. L. Broadwell and G. Becher (2010). "Changes in concentrations of perfluorinated compounds, polybrominated diphenyl ethers, and polychlorinated biphenyls in Norwegian breast-milk during twelve months of lactation." Environmental Science & Technology 44(24): 9550-9556.

Tiido, T., Rignell-Hydbom, A., Jonsson, B.A., Giwercman, Y.L., Pedersen, H.S., Wojtyniak, B., Ludwicki, J.K., Lesovoy, V., Zvyezday, V., Spano, M., Manicardi, G.C., Bizzaro, D., Bonefeld-Jorgensen, E.C., Toft, G., Bonde, J.P., Rylander, L., Hagmar, L., Giwercman, A., 2006. *Impact of PCB and p,p'-DDE contaminants on human sperm Y:X* *chromosome ratio: studies in three European populations and the Inuit population in Greenland*. Environ Health Perspect 114, 718-724.

Toft, G., Jonsson, B.A., Lindh, C.H., Giwercman, A., Spano, M., Heederik, D., Lenters, V., Vermeulen, R., Rylander, L., Pedersen, H.S., Ludwicki, J.K., Zviezdai, V., Bonde, J.P., 2012. *Exposure to perfluorinated compounds and human semen quality in arctic and European populations*. Hum Reprod 27, 2532-2540.

Trudel, D., Horowitz, L., Wormuth, M., Scheringer, M., Cousins, I.T., Hungerbühler, K., 2008. *Estimating Consumer Exposure to PFOS and PFOA.* Risk Analysis 28, 251-269.

Uhl SA, James-Todd T, Bell ML (2013) Association of osteroarthritis with perfluorooctanoate and perfluorooctane sulfonate in NHANES 2003-2008

Upham, B.L., Park, J.S., Babica, P., Sovadinova, I., Rummel, A.M., Trosko, J.E., Hirose, A., Hasegawa, R., Kanno, J., Sai, K., 2009. *Structure-activity-dependent regulation of cell communication by perfluorinated fatty acids using in vivo and in vitro model systems.* Environ Health Perspect 117, 545-551.

Vanden Heuvel, J.P., Kuslikis, B.I., Shrago, E., Peterson, R.E., 1991. *Inhibition of long-chain acyl-CoA synthetase by the peroxisome proliferator perfluorodecanoic acid in rat hepatocytes*. Biochem Pharmacol 42, 295-302.

Vanparys, C., Maras, M., Lenjou, M., Robbens, J., Van Bockstaele, D., Blust, R., De Coen, W., 2006. F*low cytometric cell cycle analysis allows for rapid screening of estrogenicity in MCF-7 breast cancer cells.* Toxicology in Vitro 20, 1238-1248.

Vestergaard, S., Nielsen, F., Andersson, A.M., Hjollund, N.H., Grandjean, P., Andersen, H.R., Jensen, T.K., 2012. *Association between perfluorinated compounds and time to pregnancy in a prospective cohort of Danish couples attempting to conceive.* Hum Reprod 27, 873-880.

Walters, A., Santillo, D., 2006. *Uses of perfluorinated substances*. Greenpeace

Wang, C., Wang, T., Liu, W., Ruan, T., Zhou, Q., Liu, J., Zhang, A., Zhao, B., Jiang, G., 2012. *The in vitro estrogenic activities of polyfluorinated iodine alkanes*. Environ Health Perspect 120, 119-125.

Wang, I.J., Hsieh, W.S., Chen, C.Y., Fletcher, T., Lien, G.W., Chiang, H.L., Chiang, C.F., Wu, T.N., Chen, P.C., 2011. *The effect of prenatal perfluorinated chemicals exposures on pediatric atopy*. Environ Res 111, 785-791.

Wang, Z., Ud-Daula, A., Fiedler, S., Schramm, K.-W., 2010. *Impact of fluorotelomer alcohols (FTOH) on the molecular and macroscopic phenotype of Tetrahymena thermophila.* Environ Sci Pollut Res 17, 154-164.

Wania, F., 2006. *Potential of degradable organic chemicals for absolute and relative enrichment in the arctic.* Environ Sci Technol 40, 569-577.

Wania, F., Mackay, D., 1996. *Tracking the distribution of persistent organic pollutants.* Environ Sci Technol 30, A390-A396.

Washburn, S.T., Bingman, T.S., Braithwaite, S.K., Buck, R.C., Buxton, L.W., Clewell, H.J., Haroun, L.A., Kester, J.E., Rickard, R.W., Shipp, A.M., 2005. *Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles*. Environ Sci Technol 39, 3904-3910.

Washino, N., Saijo, Y., Sasaki, S., Kato, S., Ban, S., Konishi, K., Ito, R., Nakata, A., Iwasaki, Y., Saito, K., Nakazawa, H., Kishi, R., 2009. *Correlations between prenatal exposure to perfluorinated chemicals and reduced fetal growth.* Environ Health Perspect 117, 660-667.

Weihe, P., Kato, K., Calafat, A.M., Nielsen, F., Wanigatunga, A.A., Needham, L.L., Grandjean, P., 2008. *Serum concentrations of polyfluoroalkyl compounds in Faroese whale meat consumers.* Environ Sci Technol 42, 6291-6295.

Weiss, J.M., Andersson, P.L., Lamoree, M.H., Leonards, P.E., van Leeuwen, S.P., Hamers, T., 2009a. *Competitive binding of poly- and perfluorinated compounds to the thyroid hormone transport protein transthyretin*. Toxicol Sci 109, 206-216.

Weiss, J.M., Andersson, P.L., Lamoree, M.H., Leonards, P.E.G., van Leeuwen, S.P.J., Hamers, T., 2009b. *Competitive Binding of Poly- and Perfluorinated Compounds to the Thyroid Hormone Transport Protein Transthyretin*. Toxicol Sci 109, 206-216.

Vested A, Ramlau-Hansen CH, Olsen SF, Bonde JP, Kristensen SL, Halldorsson TI, Becher G, Haug LS, Ernst EH, Toft G (2013) Associations of in utero exposure to perfluorinated alkyl acids with human semen quality and reproductive hormones in adult men, Environ Health Perspect, DOI:10.1289/ehp.1205118

White, S.S., Calafat, A.M., Kuklenyik, Z., Villanueva, L., Zehr, R.D., Helfant, L., Strynar, M.J., Lindstrom, A.B., Thibodeaux, J.R., Wood, C., Fenton, S.E., 2007. *Gestational PFOA exposure of mice is associated with altered mammary gland development in dams and female offspring*. Toxicol Sci 96, 133-144.

Whitworth, K.W., Haug, L.S., Baird, D.D., Becher, G., Hoppin, J.A., Skjaerven, R., Thomsen, C., Eggesbo, M., Travlos, G., Wilson, R., Cupul-Uicab, L.A., Brantsaeter, A.L., Longnecker, M.P., 2012a. *Perfluorinated Compounds in Relation to Birth Weight in the Norwegian Mother and Child Cohort Study.* Am J Epidemiol 175, 1209-1216.

Whitworth, K.W., Haug, L.S., Baird, D.D., Becher, G., Hoppin, J.A., Skjaerven, R., Thomsen, C., Eggesbo, M., Travlos, G., Wilson, R., Longnecker, M.P., 2012b. *Perfluorinated compounds and subfecundity in pregnant women.* Epidemiology 23, 257-263.

Whitworth, K. W., L. S. Haug, D. D. Baird, G. Becher, J. A. Hoppin, R. Skjaerven, C. Thomsen, M. Eggesbo, G. Travlos, R. Wilson, L. A. Cupul-Uicab, A. L. Brantsaeter and M. P. Longnecker (2012). "Perfluorinated Compounds in Relation to Birth Weight in the Norwegian Mother and Child Cohort Study." American Journal of Epidemiology 175(12): 1209-1216.

Viberg H, Lee I, Eriksson P (2013) Toxicology doi: 10.1016/j.tox.2012.12.013

Viberg H, Lee I, Eriksson P (2013) Adult dose-dependent behavioral and cognitive disturbances after a single neonatal PFHxS dose, Toxicology doi: 10.1016/j.tox.2012.12.013

Wolf, C.J., Fenton, S.E., Schmid, J.E., Calafat, A.M., Kuklenyik, Z., Bryant, X.A., Thibodeaux, J., Das, K.P., White, S.S., Lau, C.S., Abbott, B.D., 2007. *Developmental toxicity of perfluorooctanoic acid in the CD-1 mouse after cross-foster and restricted gestational exposures.* Toxicol Sci 95, 462-473.

Wolf, C.J., Schmid, J.E., Lau, C., Abbott, B.D., 2012. *Activation of mouse and human peroxisome proliferator-activated receptor-alpha (PPARalpha) by perfluoroalkyl acids (PFAAs): further investigation of C4-C12 compounds.* Reprod Toxicol 33, 546-551.

Wolf, C.J., Takacs, M.L., Schmid, J.E., Lau, C., Abbott, B.D., 2008. *Activation of mouse and human peroxisome proliferator-activated receptor alpha by perfluoroalkyl acids of different functional groups and chain lengths*. Toxicol Sci 106, 162-171.

Wolf, C.J., Zehr, R.D., Schmid, J.E., Lau, C., Abbott, B.D., 2010. *Developmental effects of perfluorononanoic Acid in the mouse are dependent on peroxisome proliferator-activated receptor-alpha.* PPAR research 2010.

Yang, Q., Abedi-Valugerdi, M., Xie, Y., Zhao, X.Y., Moller, G., Nelson, B.D., DePierre, J.W., 2002. *Potent suppression of the adaptive immune response in mice upon dietary exposure to the potent peroxisome proliferator, perfluorooctanoic acid.* Int Immunopharmacol 2, 389-397.

Yao, X., Zhong, L., 2005. *Genotoxic risk and oxidative DNA damage in HepG2 cells exposed to perfluorooctanoic acid*. Mutat Res 587, 38-44.

York, R.G., Kennedy, G.L., Jr., Olsen, G.W., Butenhoff, J.L., 2010. *Male reproductive system parameters in a two-generation reproduction study of ammonium perfluorooctanoate in rats and human relevance*. Toxicology 271, 64-72.

Zheng, X.M., Liu, H.L., Shi, W., Wei, S., Giesy, J.P., Yu, H.X., 2012. *Effects of perfluorinated compounds on development of zebrafish embryos*. Environ Sci Pollut Res 19, 2498-2505.