Nordic Council of Ministers

PFAS IN PAPER AND BOARD FOR FOOD CONTACT

OPTIONS FOR RISK MANAGEMENT OF POLY- AND PERFLUORINATED SUBSTANCES

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Xenia Trier, Camilla Taxvig, Anna Kjerstine Rosenmai and Gitte Alsing Pedersen

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Preface

The purpose of this report is to:

- Assemble the currently existing knowledge on:
  - Fluorochemicals and non-fluorinated alternatives used in food contact materials (FCMs) of paper and board (abbreviated as P&B) in Denmark, Europe, the US, and to a limited extent in China.
  - Toxicology of the fluorochemicals used and their impurities or degradation products.
  - Chemical testing of fluorochemicals.
  - Human exposure to fluorochemicals from FCMs via food, in relation to environmental exposure.
- Suggest options for evaluating the risk of fluorochemicals for which a traditional risk assessment is impossible due to data gaps.
- Present pros and cons of risk management options for fluorochemicals in P&B in the absence of a full risk assessment.

The background for the report is a Nordic workshop with international experts, which was initiated by The Danish Veterinary and Food Administration and The National Food Institute, DTU Food, to consider options for strengthening the risk management of fluorochemicals in P&B. Agilent sponsored the workshop dinner, and the report and the workshop were funded by the Nordic Council of Ministers.

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Summary

Poly- and perfluorinated alkyl substances, PFASs, are widely used substances including applications in food contact materials (FCMs) of paper and board. The substances have been found to be highly persistent, bioaccumulative and toxic, and recently some long-chain PFASs have begun being regulated or phased out. However, they have been replaced with a wide range of fluorinated alternatives that are less examined but of potential similar concern. Food is estimated to be a main source of human exposure to PFASs. However, due to the data gap in research on toxicity and exposure to these compounds, it is difficult to perform a risk assessment of individual substances, and to assess which sources are the most relevant for human exposure and hence the most effective to regulate.

The purpose of the Nordic workshop was to:

- create an overview of the use of PFASs in FCMs of paper and board, the toxicity of the different substances, and the migration of the substances from paper and board into food
- provide an overview of whether appropriate risk assessments of fluorinated substances exist and can form the basis for specific regulations or recommendations
- provide an overview of whether analytical methods suitable for analysing and regulating the substances in food simulants and/or food are available
- discuss the possibility and structure of national regulations or Nordic recommendations for PFASs in FCM of paper and board.

In conclusion of the workshop a risk management to reduce the total content of organically bound fluorine in paper and board FCMs was proposed.

As a subsequent follow-up, a level for a Danish recommended limit on total organic fluorine in paper and board FCMs was suggested by the National Food Institute, DTU Food, in 2016. The limit value should take a possible background level of fluorinated chemicals present in the paper into account. Due to higher background levels in the paper and board FCMs than originally expected and uncertainties of the analytical method, the level of the recommended limit value and the analytical method for its determination are currently under revision.

Background

Xenia Trier

Poly- and perfluorinated alkyl substances (PFAS) do not occur naturally, but have been used since the first discovery of Teflon in 1938. There was little focus on this group of organohalogens, until widespread environmental occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) was discovered about 20 years ago in biota and humans (Key 1997, Kärrman et al. 2006, Houde et al. 2006, So 2006, Lau et al. 2007, Calafat et al. 2007, Haug et al. 2009, Olsen et al. 2009, Kato et al. 2011). Prior to this, organofluorine compounds had been discovered in 1966 in the blood of production workers (Taves 1966, 1968). PFOS and PFOA, which belong to the group of perfluoro alkyl acids (PFAAs) have been found to be toxic, as have other PFAAs and precursors thereof, such as the fluorotelomer alcohols (FTOHs) and polyfluoro alkyl phosphate esters (PAPs) (Rosenmai et al. 2013). Because of their widespread occurrence, toxicity, bioaccumulation potential and extreme persistency, PFAAs and their precursors are increasingly being regulated by international regulations, such as the Stockholm Convention on persistent organic pollutants (POPs), (UNEP 2010), and the European chemicals legislation REACH (REACH 2006), and are included on the SIN list (Chem Sec 2017). In December 2016, the EU decided to restrict all use and import of PFOA (25 µg/kg) and its precursors (1000 µg/kg) in products and articles in the EU. The restriction will enter into force on 4 July 2020.

The levels of PFAAs in human blood serum are similar in Europe (Haug et al. 2009), North America (Calafat et al. 2007, Olsen et al. 2008, Kato et al. 2011), and Australia (Haug et al. 2009), but the environmental levels differ in these regions (Yamashita et al. 2005, Ahrens et al. 2009). This indicates that a western lifestyle might be linked to human exposure to PFAAs.

However, despite the ubiquity of PFAAs, the major sources for their presence in humans and the environment are not well understood. The direct sources of PFAAs include the direct use of PFAAs as the main ingredient, such as PFOA as a formerly used dispersion agent in Teflon or PFOS in hard chromeplating (Wang et al. 2014a, Dupont 2008), see Figure 1. PFAAs can, however, also stem from indirect sources, being PFAA precursors. These are typically polyfluorinated compounds, which have been shown to degrade to perfluorinated compounds, both abiotically and biotically, in the environment (Benskin et al. 2012), during processing and upon intake (D'eon and Mabury 2007, 2009, 2011, Lee et al. 2010; Butt et al., 2014). Polyfluorinated substances that are taken up from food and transformed in the body into PFAAs (Danish EPA, 2015) are examples of indirect sources. Residuals and impurities of PFAAs in other PFAS containing products, such as fluorinated FCM coatings, were previously categorized as

indirect sources (Figure 2) (DuPont 2008, Prevedourous 2006), but are recently being considered as direct sources (Buck et al. 2011, Wang et al. 2014b).

Figure 1: General information on the production and uses of perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctane sulfonyl fluoride (POSF) and fluorotelomer-based products as well as their relevance to the emissions of C4–C14 PFCAs (Wang et al, 2014 a)

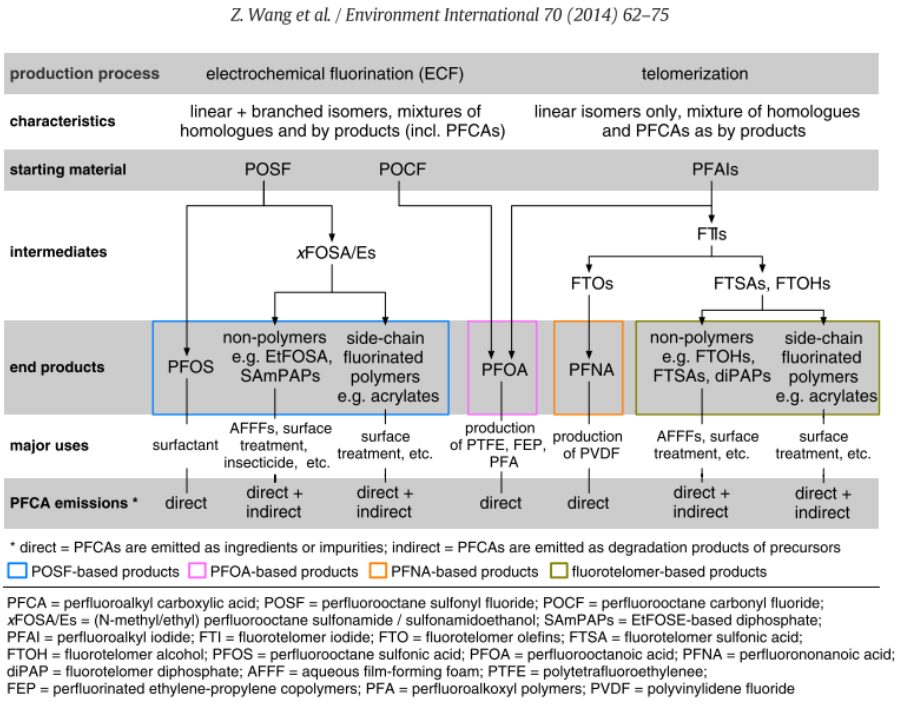
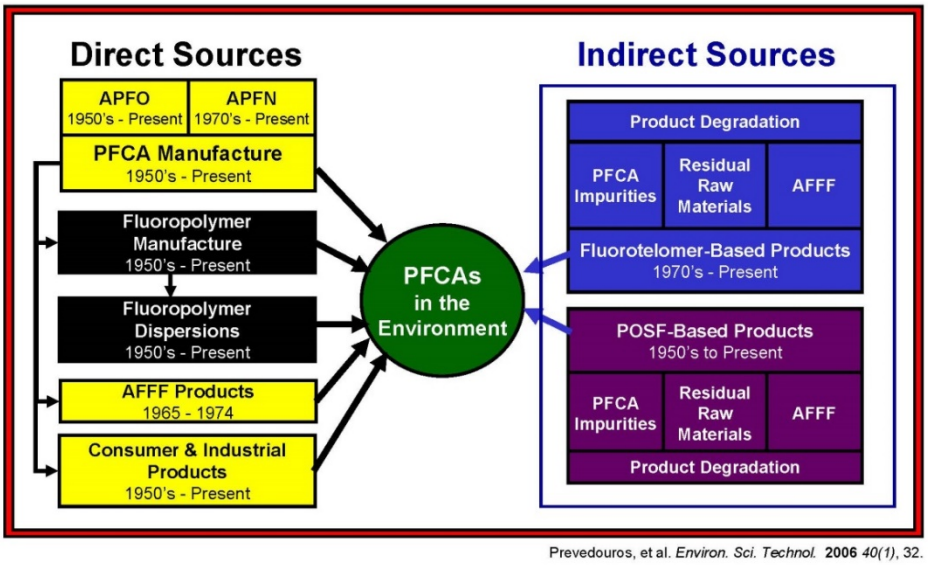


Figure 2: Direct and indirect sources of PFAAs according to Prevedouros et al, 2006



Prevedouros, et al. *Environ. Sci. Technol.* **2006** *40(1)*, 32.

Examples of widely used polyfluorinated PFAA precursors are given in Table 1, and include FTOHs and their derivatives, which degrade to form perfluorocarboxylic acids (PFCAs). In paper and board, examples are the polyfluorinated alkyl phosphate esters (PAPs), fluorotelomer mercaptoalkyl phosphate diesters (FTMAPs) (Begley et al, 2005, Trier et al. 2011) and fluorotelomer acrylates, as shown in Figure 6. Examples of polyfluorinated PFOS derivatives used in paper and board (P&B) are the alkyl-FOSEs and FOSAs, and SN-diPAPs (Begley et al, 2005, Trier et al. 2011) also called SAmPAPs (Benskin et al, 2012).

The OECD lists a total of 853 different fluorine compounds (Scheringer et al., 2014), and China has provided more than 2,000 compounds (FluoroOrganicsChina, 2013) as input to the UNEP Stockholm Convention list on POPs. Lists of specific fluorinated substances used in P&B FCMs are not available, but approximately 20–25 different types of coatings are known to be used to impart mainly fat, but also stain and water repellency to P&B FCMs. The coatings can be technical blends or polymers, and are often mixtures of homologue series of oligomers and polymers, as described in Chapter 3 on legislation. Each mixture typically contains from 3–20 structurally different molecules (Trier et al. 2011a, Trier 2011, Kissa 2001) resulting in easily more than 100 different polyfluorinated compounds. At present, only a few technical blends and polymers have had their composition elucidated (Begley et al. 2005, Trier et al. 2011a, 2011b, Trier 2011, Gebbink, 2013; Dimzon 2014). In addition, residual FTOHs and PFAA impurities are present as non-intentionally added substances (NIAS) in the technical blends used for P&B FCMs (Eschauzier et al 2012).

The TemaNord report "Per and polyfluorinated substances in the Nordic Countries – Use, occurrence and toxicology" provides a wider overview of known per- and polyfluorinated compounds used for various purposes, including PFAA precursors, which are used in or imported as part of materials and products into the Nordic countries (Norden, 2013).

Generally, most studies have focused on the measurement of PFAAs in various matrices and good, confirmatory methods exist for these compounds, which enables the estimation of their exposure from various sources. Similarly, the toxicological studies have primarily focused on the toxicity of the PFAAs (PFOA, PFOS, PFNA, PFHxA, PFBS and PFHxS) and to some extent of the FTOHs, whereas the literature is scarce on the toxicity and risk assessment of the polyfluorinated precursors of PFAAs (D'eon, 2011 a and b, D'eon 2014, Rosenmai et al., 2013, Wang et al., 2014) and other fluorinated alternatives such as the PFPEs (Trier 2011, Dimzon 2014). This data gap in both exploratory and confirmatory research on toxicity, exposure and of possibly unknown sinks of PFAA precursors makes it very difficult to assess which sources are the most relevant for human exposure—and hence whether there are a few sources which would be most efficient to regulate.

Studies on PFAAs do, however, point towards foods as being the main route of human exposure to PFAAs, with a main direct contribution from environmental pollution (Vestergren and Cousins, 2009). Major identified sources for the general population are marine foods, drinking water, red meat, and certain vegetables (Voogt, 2010), as well as fast foods (Danish EPA, 2015; Tittlemier et al. 2006; Begley et al. 2008;

EFSA, 2012). Moreover, foods and drinking water acquired around pollution hot spots might be contributing significantly to the exposure to PFAAs of the affected populations (Hölzer et al. 2008).

In P&B food packaging, polyfluorinated coatings are used to impart water and fat repellency to the paper material. Since the PFAS coatings are mainly polyfluorinated compounds, the main PFAS components in the material are indirect PFAA sources. Direct sources in the form of residuals (for PFOS) and impurities (for PFAAs, FTOHs and others) are typically also present. In relation to human exposure during the use phase of the P&B, i.e. while the food is in contact with the paper, both the polyfluorinated compounds actually used and the PFAA residuals and impurities might be significant. The typically smaller PFAAs migrate more readily into the food, and are also more easily absorbed upon ingestion. Also substances from the perfluorinated P&B coatings are absorbed in the stomach, which has been shown for PAPs in rats and in human blood (D'eon and Malbury, 2011b; Danish EPA, 2015). PFAS with weights up to around 3,600 g/mol are relevant for human uptake, since fluorine atoms are heavier than hydrogen, but the size of the molecule is approximately similar (Trier et al. 2011). Upon uptake these compounds distribute into the organism, where particularly protein rich compartments such as blood, liver, and kidneys accumulate the PFAAs. Due to their fat repellency, the perFAS (e.g. PFAAs) generally do not distribute into fatty tissues. However, this is not necessarily true for polyFAS, as supported by observations that FTOHs partition into fats (Numata et al., 2014) and into non-polar solvents (Barner, 2013), and based on theoretical considerations (Riess and Krafft 2009). This means that there might be sinks of polyfluorinated compounds in the human body which have so far not been taken into account.

In addition to human exposure during the use phase, P&B also constitute a source of exposure to humans in working-place facilities during production and to the environment during both the production and disposal phase (Scheringer et al 2014).

Whether the most relevant sources of exposure come from environmentally contaminated foods, drinking water, consumer products or food packaging, the human exposure levels for PFAAs are above a toxicological limit where regulatory action is needed to bring down the exposure (Grandjean et al 2013). To remediate environmental pollution can be very difficult and costly, whereas limiting future pollution, by limiting the use of PFASs in industrial processes and consumer products, is easier and has proven effective in the past for PFOS and PFOA. Unfortunately, the decrease in levels of some PFAAs has been followed by an increase in levels of other PFAAs, with similar persistent, bioaccumulative and toxic (PBT) properties to those they replaced—or in some cases, such as for , worse PBT properties.

This highlights three crucial points, which this Nordic workshop has focused on:

- That given the lack of a full overview of the contributions of direct and indirect sources of human exposure to PFAAs, it is relevant to regulate *all* sources that *can be* regulated. Sources related to food, such as FCMs, and drinking water are particularly relevant for regulation, since ingestion typically constitutes 80% of the human exposure to contaminants (Norden, 2013). Likewise, it is relevant to

limit the sources of PFAS from consumer and personal care products etc., and to limit pollution from contaminated sites into the groundwater. By regulating the use of PFAS, future environmental contamination of food could be reduced or avoided.

- If the restrictions focus on specific PFAS with well characterized toxicity, this may create a push towards substitution to other less evaluated PFAS. Previous examples of substitution to other chemicals have been seen, which have been costly, without sufficient improvement in the protection of human health.
- Because PFAS are persistent organic pollutants (POPs), and in several cases bioaccumulative and toxic, there is no second chance. Once PFAS are released into the environment, they will stay there and potentially contaminate the food chain for decades. Regulation that supports substitution to other persistent fluorinated alternatives must therefore be considered carefully (Scheringer et al. 2014).

Finally, future regulation of PFAS in P&B must also be practical in everyday life for its users. Since European legislation puts the onus on industries to assure safe products, in practice it is the industries who will have to manage and ensure food safety throughout the production chain for the P&B FCMs. This is typically done in a Declaration of Compliance, which is supported by analyses. The industry and the authorities both have an interest in legislation being as simple as possible and that the testing produces as unambiguous results as possible, particularly in the case of non-compliance. Both industry and the authorities will benefit from having specific regulation of PFAS in P&B, and it will also facilitate risk communication to other stakeholders, such as the public.

The aim of this report is therefore to:

- provide a (non-exhaustive) review of the current scientific basis for evaluating the toxicity of and exposure to PFAS
- discuss pros and cons for different types of limit values for PFAS in paper and board
- discuss options for the regulation of PFAS in paper and board

Sources of PFAS

Poly- and perfluorinated alkyl substances (PFAS) are man-made chemicals which do not occur naturally and which contain at least three fluorine and/or one fully fluorinated carbon group (Buck et al. 2011). Teflon is the most well-known PFAS, and was the first to be accidentally discovered in 1938, see Figure 3.

Figure 3: Timeline for the use of PFAS in the US (courtesy of A. Lindström, US EPA)

PFAS can repel water, fat and dirt, and are resistant towards aggressive chemicals and physical strain. They therefore have numerous uses in industrial and commercial products such as coatings on metal, paper, stone, leather, and textiles, in plastics (e.g. Teflon), for hard chrome plating, as lubricants, oils and waxes, dispersion agents in plastics, paints, pesticides etc., and pharmaceuticals (Danish EPA, 2008; Wang et al 2013; Norden,2013; Geueke, 2016).

PFAS have been used in paper and board food packaging since the 1950's (Figure 3), mostly as coatings to prevent the paper material from soaking up fats and water, but also in printing inks and as moisture barriers. The applications particularly target fatty foods intended to be heated in the packaging or stored for an extended period (Trier 2011). Examples include fast food paper, microwave popcorn bags, cake forms, sandwich and butter paper, chocolate paper, paper for dry foods and pet foods (Kissa, 2001, Begley et al. 2005, and 2008; Tittlemier et al. 2007; Trier et al 2011a). It is estimated that approximately 17% of foods are packaged in paper and board (Ringman-Beck 2010). The application of PFAS and alternatives to fluorinated coatings on P&B FCMs is described in more detail in Chapter 2.

Structures and names of fluorinated chemicals

PFAS are organic molecules with a carbon backbone, where the carbons form single covalent bonds to fluorine atoms. Different fields of research have varying preferences for the nomenclature of fluorocarbons. In environmental chemistry it is common to use the terms *per* and *poly*fluorinated. Fluorocarbons are *per*fluorinated if the molecules contain all C-F but no C-H bonds, and *poly*fluorinated if the molecules contain both C-H and at least three C-F bonds (Kissa 2001).

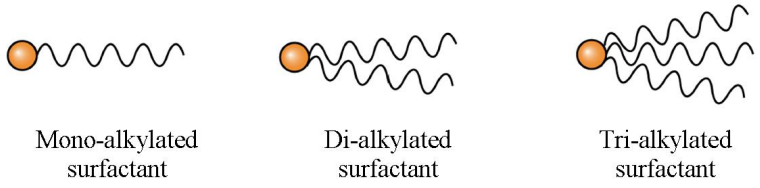
Environmental chemists prefer the notation x:y, such as 8:2 fluorotelomer alcohol (FTOH, $F(CF_2)_8(CH_2)_2OH$). For the perfluorinated alkyl acids (PFAAs) it is common to refer to only the number of fluorinated carbon atoms. As a consequence, the perfluorinated alkyl carboxylic acids (PFCA: $F(CF_2)_x$-COOH) have one less fluorocarbon atom than the perfluorinated alkyl sulfonate acids (PFSA: $F(CF_2)_x$-SO_3) in their names.

The PFCAs and PFSAs are both examples of fluorinated surfactants. These are molecules which have a hydrophilic part (also called a polar head) and a hydrophobic part, and they are classified according to these two parts, see Figure 4. The polar head can be anionic, cationic, non-ionic (at neutral pH) or amphiphilic, which depending on the pH is either ionic or non-ionic. Typical polar heads of PFAS are (Holmberg et al. 2003, Trier 2012):

- Anionic (e.g. phosphates, sulphonates or carboxylates).
- Cationic (e.g. quaternary ammonium).
- Non-ionic (e.g. poly(alkoxylates), e.g. polyfluoro polyethoxylates and glycols, acrylates).
- Amphoteric (e.g. betaines, sulfobetaines and amine oxides).

In P&B, all types of polar heads can be used in the surfactants (Appendix 1 and 4, BfR and US FDA). Surfactants are also classified according to their hydrophobic part, which may be a hydrocarbon or a poly- or per-fluorinated alkyl chain. The PFAS can function as monomers or be attached to a polymer backbone. Polymeric PFAS also include co-polymers, such as perfluoropolyethers (PFPEs), which typically have short perfluorinated chains (C_{1-4}). Other commonly used abbreviations for groups of PFAS are the fluorotelomer alcohols (FTOHs), the perfluoroalkyl sulphonamides (PFASAs), and the polyfluoroalkyl phosphate ester surfactants (PAPs). Some of the structures are shown in Figure 6 and Table 1.

Figure 4: Sketch of surfactant molecules with one alkyl chain attached (e.g. PFOA or PFOS), two alkyl chains attached (e.g. diPAPs), and three alkyl chains attached (e.g. triPAPs)



PFAS which have one alkyl chain attached to their polar head are said to be mono-alkylated, and are abbreviated to names such as 8:2 *mono*PAPs ($F(CF_2)_8(CH_2)_2O\text{-}PO_3H_2$). The di-alkylated or tri-alkylated analogues are similarly written as x:2/y:2 diPAPs and x:2/y:2/z:2 triPAPs etc.

Due to the synthesis process, the fluorotelomer-derived PFAS are present as series of homologues with an increasing number of even-numbered CF_2CF_2 units, whereas the electrochemical fluorination process used for producing the PFOS-derived PFAS result in fewer homologues separated by CF_2 units, but more branched isomers (Kissa 2001). Structural isomers, also referred to as congeners (Lee 2010), have identical elemental compositions and hence molecular weights. Examples are the different combinations of chain lengths for the di- and tri-alkylated PFAS (Kissa 2001), or the branched isomers for the PFOS-derivatives (Kissa 2001, Benskin et al. 2010). Series of homologues with several (even numbered) chain lengths, such as in industrial blends, are commonly written as $F(CF_2)_{4-16}CH_2CH_2OH$.

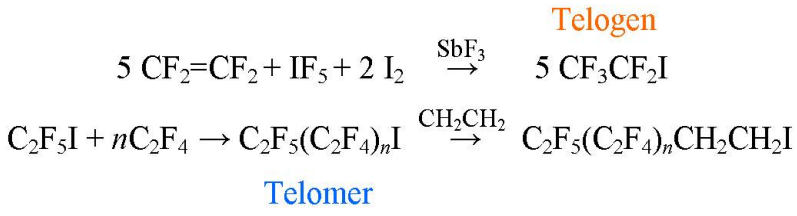
Synthesis of PFAS

In this section, some of the common industrial ways of synthesising PFAS are briefly described, to give an idea of which PFAS mixtures and impurities can be expected. Since approximately 1996 there has been a change in the environmental PFAS pattern, which points towards the fluorotelomer process being the most common synthesis method. However, in the past, electrochemical fluorination (ECF) was mainly used to produce PFOS and PFOS derivatives etc. (by 3M), and today the method has found new use in countries like China. Further descriptions of the fluorination of organic compounds can be found in (Kissa, 2001; Banks et al. 1994; Pabon and Copart 2002).

Telomerization

Telomerization was developed commercially by Du Pont Company (Kissa 2001). The process starts with the telogen, which eventually leads to a mixture of linear even-numbered carbon telomere iodides with increasing numbers of (CF_2CF_2) units, see Figure 5. Typically, the average number of $(CF_2)_n$ units is n=8 (Perrier et al. 2002, Dupont 2010). The homologues therefore have molecular weights increasing with 100 g·mole^{-1}, resulting in distinctive and easily recognizable homologue series Δm=100 Da apart in mass spectra.

Figure 5: Telomerization synthesis: The telogen is made into a telomere and into a telomere intermediate (Kissa 2001)



The telomere iodides are reacted further with ethylene to form perfluoroalkylethyl iodides, which can be readily converted to FTOHs, thiols, and sulfonyl chlorides. These are used as intermediates for fluorinated surfactants (Pabon and Copart 2002, Kissa 2001), and their derivatives, such as the FTOH derivatives, will also be mixtures of relatively many (typically 5–10) homologue series. For instance, the PAPs are made by reacting industrial blends of FTOH mixtures (e.g. Zonyl BA-L) with P_2O_5, which forms a mixture of monoPAPs, diPAPs (Pabon and Copart 2002, Kissa 2001) and small amounts of triPAPs (Kissa 2001, Trier et al. 2011a). The di-PAPs can have two identical alkyl chains attached, e.g. 8:2/8:2 diPAPs, or have mixed chain lengths, e.g. 6:2/10:2 diPAPs. The monoPAPs and diPAPs are of interest because they are used for making paper and board repellent, primarily towards oil. Acrylate intermediates, such as Zonyl TM, are other FTOH derivatives. Common to all the FTOH derivatives is that they may contain FTOH residuals and by-products of the synthesis (Eschauzier et al. 2012) as the yield is never 100% (Larsen et al. 2006).

Mixtures are often cheaper to produce, and in the case of surfactants, mixed systems often have better performance (Mele et al. 2004). Mixing different kinds of surfactants, e.g. nonionic with anionic, which have different polar headgroups, can result in non-ideal mixing and synergism with a resultant lowering of the critical micelle concentration (CMC) (Mele et al. 2004, Kissa 2001, Dupont 2010). Nevertheless, due to concern about long chain PFAS, some industries are attempting to make blends with narrower and shorter chain distributions (Lieder et al. 2009). Even so, the short-chain PFAS will contain at least 0.01% PFOA, as commented by the Fluorocouncil to the REACH proposal to regulate PFOA and PFOA precursors in materials.

Electrochemical fluorination (ECF)

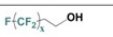
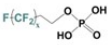
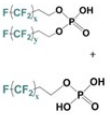
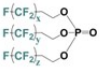
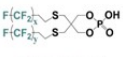
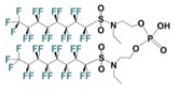
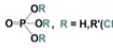
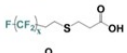
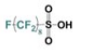
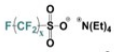
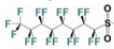
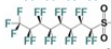
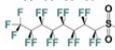
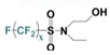
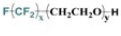
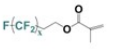
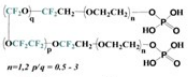
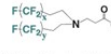
Electrochemical fluorination (ECF) is a simple method where the chemical, e.g. a carboxylic acid, is immersed into HF and a current is passed through it, which replaces all hydrogen atoms by fluorine. Yields are generally low and decrease with increasing chain lengths, where PFOA-fluoride (PFOAF) and PFOS-fluoride (PFOSF) are formed with a yield of only 10% (Gramstad and Haszeldine 1956). The synthesis by-products therefore constitute a substantial fraction of the total ECF-produced PFAS, and must be quantified to get the right picture of PFAS exposure (Vyas et al. 2007). The by-products are typically branched isomers with alkyl chains of both uneven and even numbers of carbon, which have chain lengths identical to the starting material. These mixtures of homologous linear and branched acid fluorides (PFCAF or PFSAF) are then used as raw materials to make other PFAS (Pabon and Copart 2002). The PFSAF and PFCAF derivatives might therefore have many branched isomers, but relatively few homologue series.

The unevenly numbered homologue series and the presence of extensive isomer patterns are typically used as an indication that PFAS stem from an ECF source, in contrast to the linear even-carbon-numbered chains stemming from a telomerization source (Benskin 2010; see below). However, as even numbered PFAS can be metabolized to uneven numbered PFAS (De Silva and Mabury 2006), the use of homologue series

should be used with care as a source determiner. Previously, PFOSA derivatives, such as N-Et-FOSE and SaM-PAPs (SN-diPAPs), were popular PFAS for paper and board.

Figure 6: Examples of some widely used polyfluorinated PFAA precursors and polyfluorinated PFOS derivatives

Table 1 Analytical names, trade names, uses, suppliers, structures, and which compounds we found in this study

Common name	Tradename	Supplier	Used or present as	Structure	Composition	Measured structures
FTOH x:2 fluorotelomer alcohols	Zonyl BA-L	Sigma Aldrich	Starting chemical for syntheses of fluoromonomers and polymers		$F(CF_2)_xCH_2CH_2OH$ Solvent unknown	4:2, 6:2, 8:2, 10:2, 12:2, 14:2, 16:2
monoPAPS x:2 FTOH di-substituted phosphate surfactant	Synthesised std.: no tradename [1]	U. of Toronto / Chiron*	Food paper grease/water repellent; synthesis byproduct or degradation product of diPAPS		$F(CF_2)_xCH_2CH_2OP(O)(O)(O)H_2$	4:2, 6:2, 8:2, 10:2
diPAPS x:2/y:2 FTOH di-substituted phosphate surfactant *or* Disubstituted phosphate surfactants	Synthesised std.: no tradename Zonyl NF Zonyl UR[2] Zonyl FSE	U. of Toronto/ Chiron* Sigma Aldrich / Mason/ Chiron*	Food paper grease/water repellent (incl. Zonyl NF) Mold release spray and internal lubricant (polymers); semi release (adhesives); levelling and antisoiling (caulks), (Zonyl UR) Antisoiling (paints/coatings), levelling and gloss and semirelease agent (waxes, adhesives), external lubricant (polymers), hair conditioning and rinse		$F(CF_2)_xCH_2CH_2OPO(O^-)(H$ or $NH_4^+)O)CH_2CH_2(CF_2)_yF$ + $F(CF_2)_xCH_2CH_2OPO(OH)OH$ NF: 19.5% solids; water UR: 100% solids FSE: 14% solids 24% ethyleneglycol 62% water	4:2/4:2, 6:2/6:2, 8:2/8:2, 10:2/10:2 (x+y)=12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34 (x+y)=12, 14, 16, 18, 20, 22, 24
triPAPS x:2/y:2/z:2 FTOH tri-substituted phosphate surfactant	Present in diPAPS, industrial blends and in microwave popcorn migrates	Chiron*	Synthesis byproduct of diPAPS		$[F(CF_2)_xCH_2CH_2O]_2P(O)$- $OCH_2CH_2(CF_2)_yF$	x:2/y:2/ z:2 triPAPS having diPAPS of (x+y)= 12, 14, 16, 18
S-diPAPS x:2/y:2 FTOH di-substituted thioether phosphate surfactant	Present in microw. popcorn migrates, (Lodyne P208E)	-	Food paper grease/water repellent		$[F(CF_2)_x(CH_2CH_2)_2SCH_2]_2$– $(CCH_2O(P(O)(OCH_2)$	(x+y)=12, 14, 16, 18, 20, 22, 24, 26, 28
SN-diPAPS di (*N*-ethyl-2-perfluorooctane sulfonamido ethyl) phosphate	FC 807	Danish Vet. and Food Adm.	Food paper grease/water repellent		$[F(CF_2)_xS(O)(O)N$- $(CH_2CH_2)CH_2CH_2O]_2$-P(O)OH	(x+y) = 16
Alkyl-PAPS Perfluoro alkyl organic phosphate	FF-807	Wuhan	Food paper grease/water repellent		Mixture of mono-, di- and tri-PAPS (as FC807): 100%	(x+y) = (12),14, 16, 18, (20)
3-[2-(perfluoroalkyl)ethylthio] propionate	Zonyl FSA	Sigma Aldrich	Levelling and gloss (paints/coatings, waxes, adhesives), mold release spray and $CaSO_4$ scale removal (polymers),..		$F(CF_2)_xCH_2CH_2SCH_2CH_2COOH$ 50% solids, 37.5 % isopropylalcohol, 37.5% water	x = 4, 6, 8, 10, 12
PFOS Perfluorooctanesulfonate	T-PFOS (techn. mix)	Sigma Aldrich	Starting chemical for syntheses, degradation product of PFOS derivatives		$F(CF_2)_xS(O)(O)OH$ >98%	x=8
PFSA Perfluoroalkylsulfonate, tetraethylammonium salt	FT-248	Wuhan	Starting chemical for syntheses, degradation product of PFOS derivatives		$F(CF_2)_xS(O)(O)OH$	x= 4, 6, 8, 10
PFOSF Perfluorooctanesulfonate fluoride	FX-8	Wuhan	Starting chemical for syntheses		$F(CF_2)_xS(O)(O)OF$ >90%	x=8
PFOSA Perfluorooctane sulfonamide	FOSA	Wellington	Intermediate chemical		$F(CF_2)_xS(O)(O)NH_2$ 99%	x=8
Et-PFOSA Perfluorooctane 1-sulfonamide *N*-ethyl ester	FF-09	Wuhan	Intermediate chemical		$F(CF_2)_xS(O)(O)$-$NHCH_2CH_3$ >95%	x=8
Alkyl-PFOSA[d] Alkyl perfluorooctanesulfonamide[3]	FC-10	Wuhan	Intermediate chemical		$F(CF_2)_xS(O)(O)N(CH_2)_zCH_3$)- CH_2CH_2OH >90%	x=8 z=1,2
Fluoroalkoxylate Perfluoroalkyl polyethoxylate alcohol	Zonyl FSN[4] Zonyl FSO	Sigma Aldrich	Teflon wetting aid (waxes/polishes /polymers), polystyrene coatings (coffee cups), defoamer, levelling, gloss and wetting agents Semi-release (adhesives), mold release and wetting agent (polymers), levelling, gloss and wetting agents (waxes/polishes/graphic)		$F(CF_2)_x(CH_2CH_2O)_yH$ Zonyl FSN: 40% solids; 30% 2-Propanol, 30% water Zonyl FSO: 50% solids, 25% ethylene glycol, 25% water	x=6, 8, 10, 12, 14, y= 5,6,7,8, 9, 10,11,12,13, 14,15,16,17,18,19,20
Fluoroacrylate	Zonyl TM	Sigma Aldrich	For acrylate polymers; coatings of textiles, paper, leather; UV curable coatings, fire fighting agents and emulsifier for copolymers		$F(CF_2)_xCH_2CH_2OC(O)$- $C(CH_3)=CH_2$ Solvent unknown	x=5,6,7,8,9,10,11, 12,13,14,.. (cf. *m/z* 269, 319, 369, 419, ..919 are present)
polyfluoropolyether (PFPE) di-(monophosphate)	Fomblin HC/P2 1000[5]	EU Joint Research Council (Solvay Solexis)	Food paper grease/water repellent, antistick and antiirritant in lipsticks, creams, hair conditioner Emulsifier/preservative-free systems, antimicrobial agent.	 *n=1,2 p/q = 0.5 - 3*	HO(O)(OH)PO-$(CH_2CH_2O)_n$- CH_2CF_2-$(OCF_2)_p$-$(OCF_2CF_2)_q$- OCF_2CH_2-$(OCH_2CH_2)_n$O(OH)- (O)OH, 93% difunctional content	No chromatographic separation
di (*N*-ethyl perfluoroalkyl) *N*-propanoic acid	Lodyne 2000 (aqueous dispersion)	Danish Veterinary and Food Adm.	Food paper grease/water repellent etc.	 Additional structure: Tentschert et al. 2010	$[F(CF_2)_x(CH_2CH_2)]$ $([F(CF_2)_y(CH_2CH_2)])$-N- CH_2CH_2COOH $[F(CF_2)_x]([F(CF_2)_y])C_{14}H_{23}O_6N$ Solvent unknown	(x+y)=16, 18, 20, 22, 24 (x+y) = 16, 18 (*m/z* 1138, 1238) and *m/z* 1193, 1293

[a] Can be synthesised upon request. Zonyl is a trademark of Dupont, Masurf of Masurf FS-Fluoro surfactants, Lodyne of CIBA, Fluorad FC of 3 M and Fomblin and Solvera of Solvay Solexis

[b] Other monoPAPS industrial blends are marketed under the names of, e.g. Zonyl RP; Masurf 115 and 130B; or Fluorad FC-807 and 742. FC-807 also contains up to 15% of the phosphate diester (Iengo and Pavazotti 2007)

[c] Another diPAPS industrial blend is, e.g. MASURF FS-120A

[d] In the original papers accompanying the chemical it says Alkyl perfluorooctanesulfonamide, but on the internet it says N-ethyl-N-perfluorooctylsulfonylaminoethanol

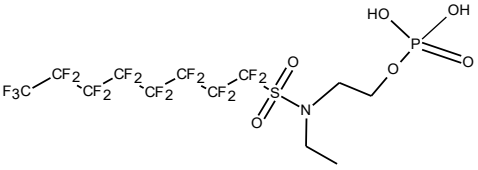
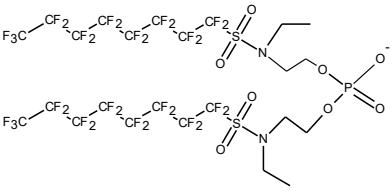
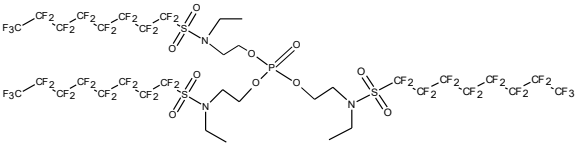
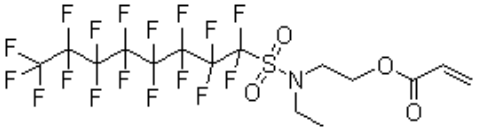
[e] Similar products are marketed as Solvera ® PT 5071, Fluorad FC-170-C and FC 760

[f] Solvay Solexis, now market a similar product called Solvera ® PT 5045a

[g] *or* Alkyl-PFOSA-OH N-ethyl-N-perfluorooctyl-sulfonylaminoethanol, there is a difference between the papers following the chemical and the description on the internet

Source: From Trier et al., 2011a.

Table 1: Examples of fluorinated surfactants, assembled with input from Trier et al 2011a and Benskin et al. 2013

Common name /Trade name	CAS No	Supplier	Structure
SaM-PAPs, SN-monoPAPs mono-perfluoroalkyl phosphate (FC 807)	67969-69-1	Before 2002: 3M Now: Quingdao (China)	
SaM-PAPs, SN-diPAPs di-perfluoroalkyl phosphate (FC 807)		Before 2002: 3M Now: Quingdao (China)	
SaM-PAPs, SN-triPAPs tri-perfluoroalkyl phosphate (FC 807)		Before 2002: 3M Now: Quingdao (China)	
N-Methyl perfluorooctane sulfonamido ethyl methacrylate		Before 2002: 3M Now: ?	residual in pre-2002 3M Scotchgard formulations
N-Ethyl perfluorooctane sulfonamido ethyl methacrylate	376-14-7	Before 2002: 3M Now: ?	monomer incorporated into Scotchgard materials
N-Ethyl perfluorooctane sulfonamido ethyl acrylate	423-82-5	Before 2002: 3M Now: ?	 monomer incorporated into Scotchgard materials
N-Methyl perfluorooctane sulfonamido ethyl acrylate (MeFOSEA)	25268-77-3	Before 2002: 3M Now: ?	monomer incorporated into Scotchgard materials

Physico-chemical properties of PFAS

Weak interactions between fluorinated chains and other molecules

Fluorocarbons have limited ability to form bonds with themselves or other molecules for a number of reasons. The atomic radius of fluorine (1.47 Å) is comparable in size to a hydroxyl group, which is larger than hydrogen (1.20 Å) but smaller than chlorine or bromine. The size of fluorine is just right to pack closely around a carbon chain and shield it from interaction with other atoms, as shown in Figure 7. Furthermore, the carbon backbones are shielded from attack because fluorine, as the most electronegative atom in the Periodic Table, is unpolarizable. For the same reasons, fluorine in C-F systems is unable to make hydrogen bonds (Krafft and Riess 2009). The limited ability to form bonds also gives fluorocarbons unexpectedly higher vapour pressures compared to corresponding hydrocarbon molecules (Kissa 2001).

This section goes into detail about the physico-chemical properties of PFAS, to give an understanding of why PFAS behave so uniquely, both in relation to their persistency and their adhesiveness to surfaces and to proteins. Since fluorinated alternatives might share many of the same technical properties, they might also share some of the same toxicological properties and persistency, which should be taken into consideration during their approval.

It is the unique properties of PFAS, such as high surface activity, water and oil-repellency and weak intermolecular interactions, which are responsible not only for their usefulness in technical and consumer applications, but also for their behaviour in the environment and other biological systems.

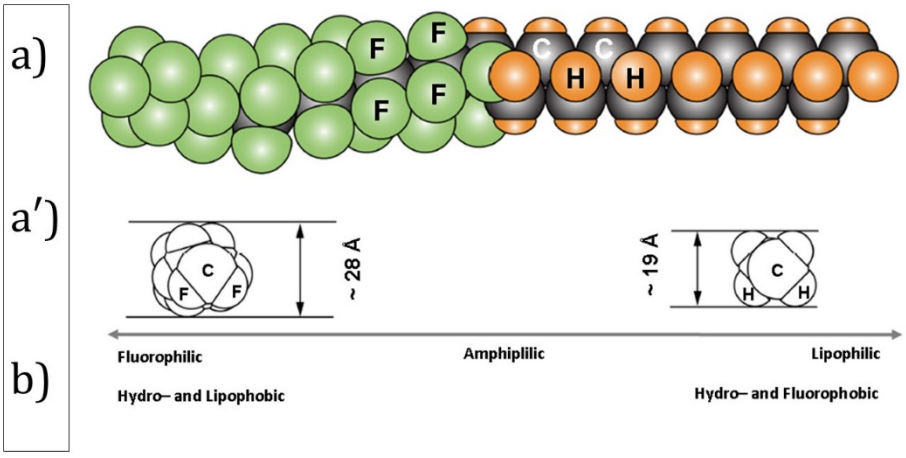
Meanwhile, these characteristics also pose some challenges for their analysis, which must be considered during method development. The fluorinated segment of PFAS, for instance, is repelled both by purely aqueous solvents (it is hydrophobic) and pure hydrocarbons such as oils (termed oleophobic) or fats (termed lipophobic). Only a few studies have investigated the influence of the physico-chemical properties of PFAS on analytical methods (Begley et al. 2005, 2008, Ropers et al. 2009).

Resistance towards degradation of the fluorinated chain

The high electro-negativity of fluorine makes the C-F bond shorter and stronger than C-H, C-Cl or C-Br bonds, which together with the perfect packing of the large fluorine atom also make the perfluorinated alkyl chain more rigid (Krafft and Riess 2009). The strength of the C-F bond also affects the adjacent bonds, so that the F_3C-CF_3 bond, for instance, is 10 kcal mol^{-1} stronger than the H_3C-CH_3 bond (Banks et al. 1994). Finally, the ionization energy required to extract a fluorine atom (F^-) from PFAS is high due to the high bond energies and the low polarizability of fluorine, and because fluorine is such a poor leaving group (Grainger et al. 2001, Kissa 2001). The difficulty in ionizing or breaking the fluorocarbon backbone therefore make PFAS more resistant towards most chemicals (such as acids and bases), heat or abrasion. For these reasons, PFAS are

useful for high temperature applications, such as when the food and packaging are intended for heating in a microwave oven.

Figure 7: An example of a linear FnHm diblock containing a fluorinated chain and a hydrogenated chain

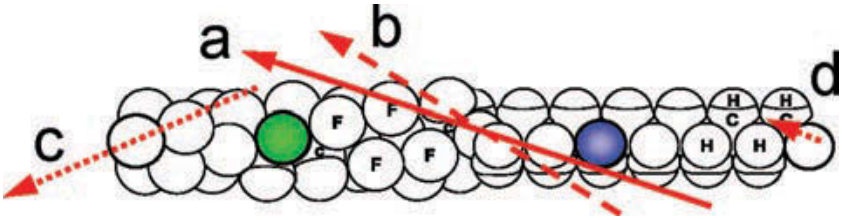


Note: This renders the molecules (a) Amphisteric; i.e. with a different twist of the chain (a': Cross Sections of the F- and H-Blocks) and (b) Amphiphilic, i.e. with different solubilities.

Source: Krafft and Riess 2009.

However, at the point where the fluorocarbon meets the hydrocarbon, dipoles are created, with the consequence that a *poly*fluorinated molecule can interact or bind via dipole bonds.

Figure 8: F-Alkyl/H-Alkyl diblocks host a strong dipole



Note: (a), with components arising from (b) the FnsHm junction, (c) the terminal CF_3, and (d), to a much lesser extent, the terminal CH_3.

Source: Krafft and Riess 2009.

Architecture of PFAS polymers

In light of the bioaccumulation of longer chain PFAS, fluoropolymer surfactants containing shorter fluorocarbon segments are being put forward as alternatives. To achieve the same grease-repellency, the polymer needs a carefully designed structure or "architecture', which is described below.

The effect of fluorine can be maximized to achieve a low surface energy if fluorocarbon segments are placed on the end of hydrocarbon chains (Pabon and Copart 2002). The further the fluorocarbon chains are situated away from the hydrocarbon

chains; the better the solubility of the PFAS in hydrocarbon solvents (Krafft and Riess 2009). Exactly where the fluorinated moieties are situated in the polymer greatly influences its surfactant properties. This potentially enables the use of shorter perfluorinated chains to achieve the same technical performance or even improved surfactancy compared to fully fluorinated PFAS. These so-called mixed surfactants, which contain both a fluorinated and a hydrogenated part, are also more compatible with hydrocarbon solvents and matrices, which can be useful for printing for example, where a fluorinated surface layer must be compatible with hydrocarbon based inks and lacquers. The non-ionic polymeric PFAS are also less sensitive to precipitation with salts or other surfactants, and can therefore withstand high pH (e.g. during the paper production process).

A great number of polymerization methods are available, which enables a number of strategies for the incorporation of fluorine into polymers. The resultant fluorinated chains are generally anchored as side chains from the main polymer chain, and can be introduced by a variety of linking units (Pabon and Copart 2002). Common for polymers prepared from FTOH intermediates is that they have a $F(CF_2CF_2)_n(CH_2)_2X$ chain, where the X is a hetero atom, such as O, N, S etc. (Turri et al. 2000). Fluoro-acrylate resins are used, for example, as glue in microwave susceptors, which are the aluminium sheets in paper bags that heat up during microwaving (US FDA 2010a, 2010b), and fluorinated acrylate polymers (e.g. Foraperle, Kelley 1991, 1998) are used for food paper and board. The polyfluoroalkoxylates have a terminal FTOH chain attached to a polyether of homo- or hetero alkoxylates (homo- or hetero co-polymer), where the non-ionic ethoxylates $F(CF_2CF_2)_x(CH_2CH_2O)_yH$ are examples. These PFAS are, for example, also used in FCMs as lubricants (Dupont 2010), and have been patented as "retention-aids" on expanded polystyrene coffee cups, to prevent the cups from leaking as the styrene cups deform due to the heat (Sonnenberg 1987).

In other cases, the polymer backbone itself can be the fluorinated portion of the macromolecule. The perfluoropolyethers (PFPEs) thus contain perfluorinated ether units of typically $O(CXF)_{1-3}$, where X can be F, H or Cl. They are typically co-polymerized with alkoxylate units $O(CH_2)_{1-3}$. An example is the Fomblin HC/P2–2000 from Solvay Solexis. The synthesis and surfactant properties of PFPEs have previously been described (Szymanowski 1993, Matuszczak and Feast 2000, Turri et al. 2000).

The PFAS described here are just a fraction of the existing PFAS, being >5000, as advertised by a US company (Indofine 2015). However, as the FTOH-derived PFAS dominate the US FDA and the BfR lists of approved PFAS for food paper coatings, they constitute a solid starting point for the analysis of PFAS in food paper (Appendices 1 to 8).

In conclusion, on the basis of the physical chemistry of the PFAS, it is not scientifically valid to assume that per and poly FAS behave similarly. As an example, the perfluorinated AAs do not accumulate in fats, whereas it is likely that polyfluorinated AA precursors have some ability to mix with hydrophobic compartments. This means that poly FAS could be present in hydrophobic or fat sinks, from where PFAAs can be released. In addition, the fluorinated alternatives, such as the perfluoropolyethers (PFPEs), might have very different behaviour in the

body and hence different toxicity, such as mixing into and blocking the cell membranes, which is used pharmaceutically.

Persistent, Bioaccumulative and Toxic

Most of the characterized PFAAs are persistent, bioaccumulative and toxic (PBT chemicals), which are three properties that are a particular cause for concern.

PFAS are persistent because the fluorocarbon chain is inert to degradation in humans, biota, and other environmental matrices. The persistence of such a chemical implies that it "has time" to be distributed over long distances and eventually cause global contamination.

Some PFAS are also bioaccumulative and bind in biota and humans to proteins, rather than to fats. The reasons for this are not yet fully understood, but are likely related to their surfactancy combined with their lack of solubility in both water and fat. As a result, they tend to reside inside cavities, such as serum albumin. The short chain PFAAs are much more water soluble and less bioaccumulative in humans and biota, but still stick to protein surfaces. They also accumulate in plants, possibly due their water solubility, resulting transport in the plant, and subsequent evaporation of the water from the leaves. In surface water, the concentrations of short chain PFAAs are rising because they cannot be removed by traditional water treatment methods. This is strictly speaking not bioaccumulation, but it has the same effect of rising concentrations in the water compartment. The bioaccumulation potential implies that even the very low concentrations in ocean water that result from environmental long-range transport of such substances, build up to much higher concentrations in the tissue of organisms such as fish, seals, whales, birds, and also humans.

Many of the PFAS have toxic properties, as described in Chapter 6. The toxicity of the PBT substances means that even relatively low levels are sufficient to cause adverse effects in organisms. A further implication of the PBT properties is that there are no safe levels for such chemicals, because the bioaccumulation process can start even from very low levels. Even if it takes months or years for toxic concentrations to build up in organisms, this is possible because of the high persistence of the substances.

1. Use and presence of fluorochemicals in P&B

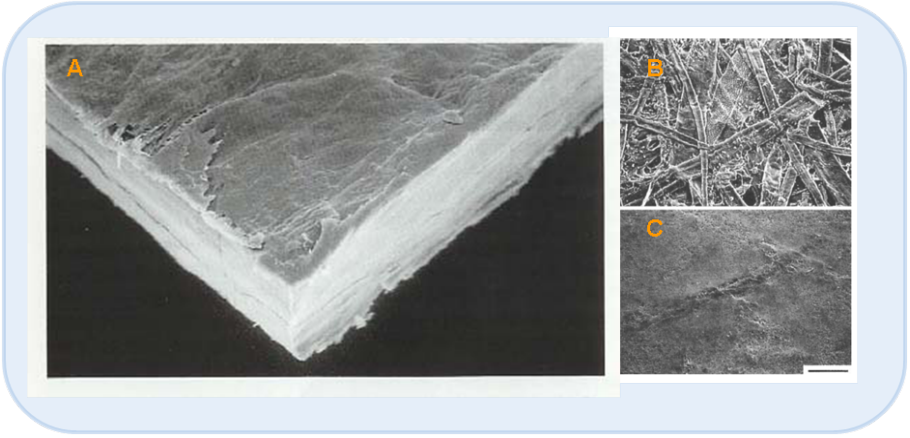
Xenia Trier

1.1 Strategies to make paper and board packaging repel food

There are generally two types of barriers against grease or fat for paper and board. These are a physical barrier or a chemical barrier. For a physical barrier in the paper, the paper structure itself will serve as an obstacle to grease penetrating the paper. A chemical barrier is added to the paper and will repel grease due to the decreased surface energy of the paper surface (Yang et al., 1999). This type of barrier can be achieved either by addition of chemicals to the pulp (Perng and Wang, 2004) or as a surface treatment of the paper or board.

Liquids can soak into paper and board material either if the cellulose fibres are wetted, or if liquid is drawn into the capillary pores. There are two strategies for making the material repellent: making a barrier on the surface or creating a low energy surface. Traditionally, liquid uptake was prevented by the production of narrow pores, which was achieved by making cellulose fibres very fine (microfibrillated) and cross bonded, for instance by beating (see Figure 9 A), or by using sulphuric acid to make parchment. Today, it is common to make a barrier by laminating an extra layer of plastic or aluminium onto the material. The disadvantage is that the machines must have laminating facilities and the material is difficult to recycle. Instead, chemicals can be used, by coating the fibres to prevent them from being wetted (internal and external sizing, see Figure 9 B), by filling the pores (coating, see Figure 9 C) or by coating the whole surface with a film. PFAS can be used as an internal and external sizing agent, and in a surface coating.

Figure 9: Environmental Scanning Electron Microscopy (E-SEM) picture of a greaseproof paper structure, showing the tightly sealed surface of the paper. The absence of macroscopic pores is due to extensive beating, which produces large amounts of highly hydrated fines and very collapsed fibre walls



Note: Scanning electron photomicrograph of the surfaces of B) surface sized and C) coated paper. Scale bar : 50 µm. The illustration is modified from The Chemistry of Paper, Roberts (1997).

Source: The illustration is modified from an illustration by Prof. Christer Fellers (From Aulin 2007 thesis).

The term "sizing" is somewhat ambiguous, as it covers two phenomena: internal sizing prevents (or retards) a liquid from penetrating the body of the paper, whereas external sizing prevents penetration of the surface layer. Whether the PFAS is used at the surface layer, or permeates all the way through the material, will influence the distance the PFAS must travel to reach the food, and therefore how fast the PFAS is transferred to the food. Since PFAS can make paper of very uneven fibres (Figure 9 B) repellent, they are used in applications such as recycled paper consisting of mixed fibres.

1.1.1 Internal sizing

Internal sizes, also called sizing agents, such as PFAS, are usually added as waxy particles of approximately 1 µm to the pulp. This is why they are said to wet-end coat the paper. In this way, they will be retained in the paper web without interfering with the crosslinking of the cellulose. During the pressing and drying process of the paper, the wax melts and the sizing agents migrate into the body of the paper and coat the fibres (Roberts 1996). Faster migration (diffusion) rates are obtained if the molecules are small, which could be one reason why many of the PFAS were originally monomeric instead of polymeric surfactants.

After reaching the fibre, the sizing agent (i.e. the surfactant), orients itself perpendicular to the fibre surface, creating a low energy (difficult to wet) surface (Roberts 1996). For the orientation to occur, the surfactant must either form a strong electrostatic bond to the paper, or be bound covalently to the surface. Cationic sizes will be attracted to the anionic surface of the paper, and possibly anionic sizes can be attracted to cationic additives and fillers. More often, the sizes are bound directly (chemisorbed) to the surface by forming an ester bond with the hydroxyl groups of

cellulose. The commonly used non-fluorinated Alkenyl Succinic Anhydride (ASA) and Alkyl Ketene Dimer (AKD) are examples of this reaction, which proceeds at neutral to high pH (Roberts 1996). Very little information is available in the open literature on how and by which mechanism (chemisorption or physical adsorption) the PFAS bind to paper surfaces (Aulin et al. 2008). Nevertheless, Aulin et al. mention that perfluorodecanoic acid (PFDA) was covalently bound to cellulose. It therefore seems likely that the polyfluoro-carboxylates, but also phosphates and sulphate PFAS sizes, can form ester bonds with the cellulose hydroxyl groups, for example through a Fisher esterification. This requires a catalyst and heat to remove water, which is supplied during the drying of the paper (Smith and March 2007). Given the reversible nature of a Fisher esterification, the PFAS could potentially be released upon hydrolysis of the ester, for instance if the paper got in contact with nucleophilic water or alcohol. This requires, that the nucleophile gets in close contact to the carbonyl, phosphonyl or sulfonyl group, and hence that the solvent has a lower surface tension than the sized paper to wet the surface. While this is not possible for water at room temperature, higher temperatures and alcohols might wet the paper. This could also explain why the German BfR and the US FDA exclude certain PFAS, such as the PAPs from contact with alcoholic foods. BfR has removed PAPs from their recommendation list precisely because they were too prone to hydrolysis and hence migration to food, for example during food preparation.

Flexible papers, which have a high cellulose content, require up to 10 times as much sizing agent and are more difficult to size for reasons that are not fully understood (Roberts 1996). Furthermore, for the bulk of the paper materials, coating requires more sizing agent than what is required for sizing a surface layer of the paper. It can therefore be expected that thin, flexible papers with high cellulose contents, and which are internally sized, contain more PFAS and hence have a higher migration potential.

Internal sizes have the advantage that even if the fibres are exposed to water or fats from, say, chocolates, they will not be wetted. In addition, the paper will maintain a more "natural" look compared to a shiny plastic or varnish surface, or the glassy look a traditional "acid sizing" parchment method produces. The downside of internal sizing is that it requires more sizing agent to coat the fibres of paper, say 100 µm thick, than to apply a surface layer of a few µm. This imposes a higher risk of migration of PFAS during the use phase.

1.1.2 External sizing

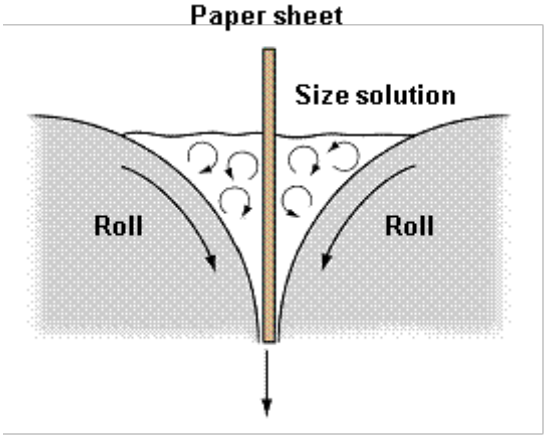
External sizes can be added after the production of the paper, which is why the process is called dry-end coating (Roberts 1996). This gives greater flexibility in the production (Dupont 2010). External sizes can be applied directly as surface coating films, or be mixed in with varnishes, also called lacquers. Both form a protective surface layer which prevents wetting of the fibres and suction of liquids into the pores of the paper. Figure 10 shows how the coating can be applied to the paper. To make a uniform coating without holes, the size must adhere to the paper and not to the rolls, which requires that the viscosity of the size formulation is sufficiently low. Low viscosity can be

achieved using dilute solutions, but then more solvent must be removed after application, which prolongs the drying step. Instead, small sizing molecules can be used as they give lower viscosity than polymeric sizes. For externally sized paper and board, there is also a technical argument for using small molecules as sizing agents. PFAS in external sizes can therefore also be expected to be monomeric unless they are applied as a polymeric layer.

Polymeric PFAS layers can be applied on boards using the hot steel drum method, as described for the polyacrylate PFAS named Foraperle by Dupont (2010). In this method, a surface layer of lacquer is applied and pressed against a hot steel drum, which gives the surface a high gloss.

A frequently used coating method for the coating of greaseproof paper is the size press, in which a coating is applied on the surface of the material. Today, general guidelines for dosages of fluorochemicals for surface treatment could be in the range of 0.2 up to 1.0 wt% solid on paper.

Figure 10: The hydrodynamics of external sizing, where a low viscosity of the size solution is preferable for production



Source: Inspired by Roberts (1996), p. 144.

A coating technique similar to the size press is the Metering Size Press (MSP), which consists of two rolls (transfer rolls) in contact with each other on which a pre-metered amount of the polymer solution is dosed, usually with a smooth or wire-wound rod. The polymer solution is transferred to the paper in the nip between the transfer rolls, and the two sides of the paper can be coated simultaneously. The MSP has replaced the size press in high speed paper machines and is now the most frequently used process for surface sizing paper (Klass, 2002). An aqueous polymer solution, such as a starch solution, is used with these coating techniques by the paper industry today. The coating technique is the same whether PFAS are added to the starch solution or not.

A disadvantage of surface coatings (external sizes) is that the coating can crack, whereby liquid can seep in and blot the paper. This is likely to happen for foods with long storage times which are packaged in thin flexible paper, because the packaging can be easily and repeatedly creased when handled in the supply chain, in the shop, or by the consumer. The high temperatures paper for microwavable food etc. can be

exposed to also damage a thin surface coating, for instance by melting and making pinholes in the coating.

1.1.3 Types of sizing agents

In the 1970s there was a switch to an alkaline production process, due to problems with degradation of the paper material at acidic pH, and because the calcium carbonate filler, which allowed filler contents up to 30%, could not be used at acidic pHs. Sizing and coating chemicals which are compatible with the currently used neutral or alkaline pHs include various PFAS sizes and non-fluorinated alkyl ketene dimers (AKD), alkenyl succinic anhydride (ASA) (Roberts 1996), styrene–acrylic copolymers (Yeates et al. 1996), talc-filled water-based polyacrylate (Rissa et al. 2002), pigment-filled hydrophobic monomer dispersions (Vähä-Nissi et al. 2000, 2006), polyvinyl alcohols and montmorillonite/polyethylene-coatings (Krook et al. 2005), modified wheat protein, and silicones. Silicone treated paper, used for products like baking paper, is also water repellent but not fat-repellent, but the silicone will let the baked goods release from the paper. In contrast, PFAS treated paper has the advantage of being both oil and water-resistant, which makes it useful for multipurpose food packaging materials.

The fluorinated coatings and sizing agents that are approved by the German BfR (Appendix 1) and the US FDA (Appendix 4) include PAPs, fluoroacrylates (Huber and Yandratis 1998), carboxylic acids, phosphoric acid esters and polyurethane derivatives of PFPEs (Solvary-Solexis 2010). Common for the commercial PFAS which are used for paper and textiles (that both can contain cellulose) is that they typically contain several fluorinated alkyl chains or repeat units (Kissa 2001, Schultz et al. 2003, Schröder et al. 2003, 2005, Krishnan et al. 2005, Dinglasan-Panlilio and Mabury 2006, Sáez et al. 2006, Jensen et al. 2008b, Washington et al. 2009, Riess 2009, Russell et al. 2010, Quinete et al. 2010, and patents: Grollier et al. 1981, Kelley 1998, Huber and Yandrasits 1998, Kantamnemi 2004, Haddad et al. 2005, Guerra et al. 2007, Iengo and Pavazotti 2007, Turri et al. 2000, 2008). The concentration of the fluorochemical is typically allowed to range from 0.2 to 1.5% of the paper (see Appendices 1(BfR), 4 (US) and 8 (Chinese)), whereas the technical application papers accompanying industrial blends mention concentration ranges from 0.1–4% (Dupont 2010, Ciba-BASF 2000–2010, Iengo and Pavazotti 2007). In the US FDA legislation, the maximum quantity of mono and di-PAPs in paper and board was earlier set to 8.3 mg dm-2 (17 lbs·1000 ft-2) (US FDA 2010b). Appendices 1–8 show that the number of PFPEs and fluoroacrylates are well represented. Also fluorinated oximes and polyurethanes are used, as well as the former 3M manufactured PFOSA derived N-Me- and N-Et-FOSEs (called alkyl-FOSEs, Wuhan Fengfan 2010, Qinhuangdao Bright Chemical Co. 2011) and alkyl-FOSE-phosphates (SN-diPAPs alias SaM-PAPs or FC 807, previously marketed as Scotchban, sold by 3M) which are now sold in China by Qinhuangdao Bright Chemical Co. (2011).

Lists of PFAS used in paper and board have been assembled from the ESCO list (EFSA, 2011) and from national P&B lists. The types of PFAS and the levels and frequency of use in Danish paper and board packaging have been changing since 2007 (Trier et al. 2011a, DVFA, 2013; DVFA, 2015). Also in Norway, recent reports show that

PAPs coatings are no longer used, but instead FTOHs are found, probably because residuals and degradation products of the fluorochemicals applied to the paper (Blom and Hanssen 2015). Both analyses and declarations of compliance (DoC) point towards some degree of substitution to other fluorinated alternatives and so-called short-chain fluorochemicals (e.g. perfluoropolyethers and C6 based fluoroacrylates), as well as to non-fluorinated sizing chemicals (e.g. silicones) and physically sized materials, such as the traditional parchment paper.

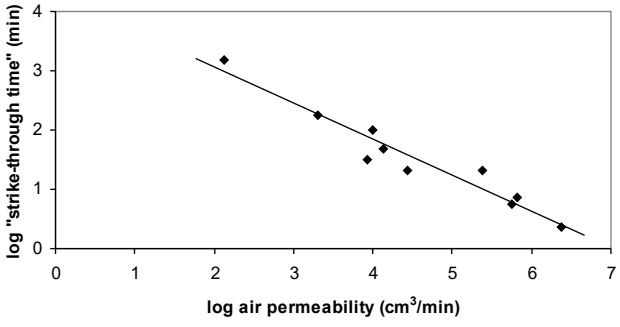
1.2 Alternatives to fluorochemicals as coatings in paper and board FCMs

1.2.1 Physical barriers

Various alternatives to the use of fluorochemicals for creating barrier properties in paper and board exist. Two of the most common types of paper with an intrinsic mechanical barrier against grease are natural greaseproof paper and vegetable parchment. These two materials both have a dense cellulose structure that provides the grease resistance.

In the production of natural greaseproof paper, refining the fibres results in the dense structure of the paper. Refining makes the fibres flexible and makes it easier for them to come into intimate contact with each other so that they can bond to each other. The greater the refining, the closer the fibres come to each other (the higher the density of the final paper) and the greater the contact area between them. As a result of the densification of the paper, air permeability and light scattering are reduced. The relationship between air permeability and grease resistance for greaseproof papers was presented by Corte (1958) and is shown in Figure 11. Additional effects of the refining are that the refining increases the tensile and burst strength of the paper while tear strength is reduced.

Figure 11: Comparison of grease resistance and air permeability



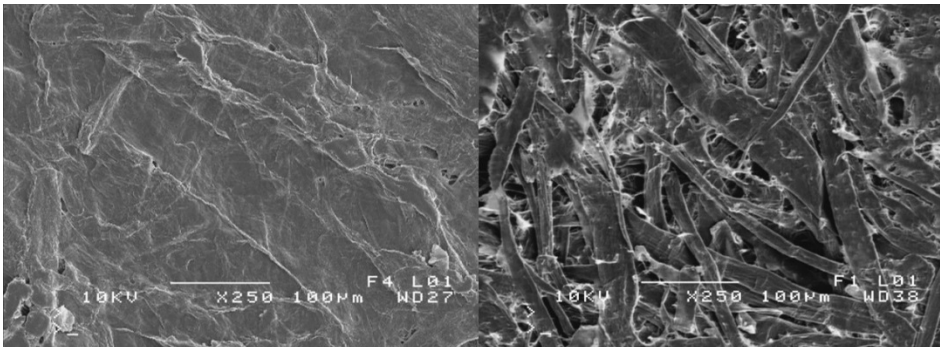
Source: (redrawn from Corte, 1958).

Vegetable parchment initially has a fairly open structure, but when the paper is passed through a bath of concentrated sulphuric acid, the cellulose fibres react with the acid and almost melt together (Twede and Selke, 2005). The reaction between the acid and the cellulose is interrupted by dilution with water and the paper sheet is finally consolidated by a drying process. This treatment results in a paper with high air resistance. The sheet structure is dense with a small number of pores (Giatti, 1996). Vegetable parchment offers a very high barrier to water and fat (Knox et al., 1977).

The structural difference between a non-fluorinated natural greaseproof paper and a fluorocarbon treated paper is illustrated in Figure 12 below (Kjellgren, 2007). The greaseproof paper has a dense surface structure created from cellulose, which provides the barrier against grease. The fluorocarbon treated paper has a more open paper structure, but in this case the added chemicals provide a grease repellent surface.

Grease resistant packaging is used for fatty foodstuffs (e.g. baking paper and muffin cups), but also to provide water barrier properties (e.g. baking papers in contact with frozen dough or microwave popcorn bags). Silicone can be added to achieve release between the paper and the baked goods and to improve the water repellency (but not the fat repellency) of the paper surface.

Figure 12: Surface of an uncoated natural greaseproof paper (left) and a fluorocarbon-treated paper (right)



Source: presentation by NordicPaper, 2015.

1.2.2 Chemical barriers

To improve the barrier properties and reduce the air permeability, greaseproof papers are typically coated with starch, carboxymethyl cellulose (CMC) or polyvinylalcohol (PVOH). Starch closes the surface of the paper and reduces the air permeability, and can in this way also improve the coating hold-out of additional coatings (Kjellgren, 2005. Other non-fluorinated coatings used to improve the grease resistance of paper and board could be aqueous dispersions of copolymers (styrene and butadiene), aqueous dispersions of waxes, or water soluble hydroxyethylcellulose (HEC), as given in Table 3 below. Coating can be an economical alternative to refining to achieve certain air permeability (Kjellgren and Engström, 2005). In addition, greaseproof paper can be coated with a functional coating. Silicone is used primarily as a release agent but also gives the paper a water repellent surface.

Another example of a coating that can be used to improve grease resistance is chitosan (table 2).. Several studies on paper have been made using chitosan to study its potential to provide a grease barrier, and barriers comparable to those obtained with fluorinated resins have been achieved (Ham-Pichavant et al., 2005; Kjellgren and Engström, 2006).

Table 2: List of various coating alternatives to PFAS

Type of alternative coating:
Starch
CMC
PVOH
Wax dispersions
HEC (hydroxyethylcellulose)
Copolymer (styrene-butadiene)
Chitosan
AKD (Alkyl Ketene Dimer)
ASA (Alkenyl Succinic Anhydride)

1.2.3 Other barrier materials

Plastic and aluminium are two other types of barriers that can be used instead of mechanical treatment of the paper and chemical coatings. A concern that has been raised is that paper material coated with plastic or aluminium on the food contact side (as for milk cartons) instead of fluorochemicals, can hamper the recyclability. While it is certainly true that non-biodegradable plastic and aluminium will slow down composting while fluorochemicals will not, it is also not desirable to have fluorochemicals mixed into the compost, and crops then growing in contaminated soil. This has been the cause of drinking water contamination, both in Germany (Hölzer et al. 2008) and in the US, according to US EPA measurements and a presentation at the Nordfluor 2013 workshop.

1.2.4 Consequences of alternatives to fluorochemicals

It is clear that there are commercially available techniques that are alternatives to the use of fluorochemicals in paper and board, as has been exemplified by the substitution by COOP Denmark A/S, a Danish consumer goods retailer, in all their own products since September 2014.

The US FDA has reached a voluntary agreement with the manufacturers of C8 perfluorochemicals subject to Food Contact Notifications (FCNs) not to sell those products into food contact applications see (http://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/Notifications/ucm308462.htm). Market forces and environmental requirements from the US Environmental Protection Agency have basically eliminated the use of the C8 perfluorochemicals listed in the Code of Federal Regulations (CFR). The US Food and Drug Administration (FDA) is in the process of removing those listings from the CFR, but this takes time.

As elaborated in Chapter 8 on risk management, there are a number of well-established business cases showing that non-fluorinated alternatives are:

- available and functional for all uses of paper and board FCMs intended for different foods
- cost-neutral for retailers and hence most likely also for manufacturers
- safer to use from a food safety point of view—provided that the alternatives are tested for safety
- a more sustainable alternative, since they do not expose workers, the environment, or consumers to persistent chemicals during the production, use and disposal phases of the paper and board material.

However, there are some differences in the production of PFAS-free materials, such as natural greaseproof paper, compared to paper with fluorochemicals. The refining of the fibres in the production of greaseproof paper results in swelling of the fibres. A consequence of this is that the dry solids content, before entering the press section in a greaseproof paper machine, is low for greaseproof paper—typically 15% (Stolpe, 1996), compared to 20% for other plain paper grades (Fellers and Norman, 1998). This paper will thus require longer time to dry off the water in the fibres. The machine speed is therefore slower on the machines that produce natural greaseproof paper compared to those which produce paper with fluorochemicals. This results in a higher cost for natural greaseproof paper compared to paper treated with fluorochemicals.

1.3 Background levels of PFAS from other sources

No scientific investigations are available on the possible PFAS contamination of paper and board FCMs if contaminated processing water is used in the paper manufacturing. PFAS are ubiquitously found in the aqueous environment, with concentrations usually ranging from pg to ng/L for individual compounds (Ahrens, 2009). The background levels of PFAS in Danish surface and ground water has been estimated to be < 0.03 µg/L (Norden, 2013). A review by Stahl et al. reported the level of PFAS in tap water from various countries, e.g. 0.13 µg/L in tap water from China (average level of PFAAs in Shanghai), whereas a much lower level of 0.00062 ug/L was found in tap water from Japan (Stahl et al., 2011). Higher levels of PFAS can occur locally, e.g. close to wastewater outflows from factories using PFAS, as observed in Italy and in the US. It is likely that non-intentionally added PFAS from processing water can bind to the paper, particularly the long chain PFAS (containing > 5 fluorocarbons), as it has been shown for their adsorption into active coal and sludge in wastewater treatment plants (Eschauzier et al. 2012).

Another source which could contribute to a background level of PFAS is recycled paper, dispersion aids in colorants and pigments, other chemicals used in the process (e.g. lubricants in the machines), or detergents used to clean the machinery. Again, no

scientific studies have measured or evaluated the possible contribution of each source of background contamination of PFAS in paper and board, but the above mentioned uses are described by UNEP (2009) and Kissa (2001). An estimate of a possible background level can be attempted based on the results from four Danish paper and board studies conducted at DTU Food since 2009 (sampled 2009 (Trier 2011), 2010 (DFVF, 2011) 2011–2012 (DFVA 2013), 2013–2014 (DFVA 2015) (Jensen, 2014). These show that there is a group of samples which have low PFOS levels, from <LOD to approximately 0.05 µg PFOA eq./g paper, corresponding to approximately < LOD to 1 ug PFOA eq./kg food. However, since the analysis method at DTU Food specifically measures for a selection of PFAS, other PFAS that are not included in the methods could be present. In the 2015 study, all samples were additionally analysed for total organic fluorine and the results ranged from <LOD to 455 µg/dm^2 of paper. To get better values for the background levels of PFAS in paper and board, further samples of particularly non PFAS treated paper and board samples must be analysed using the total organic fluorine method, as described in Chapter 4.

2. Existing legislation for fluorochemicals in P&B

Xenia Trier [1]

This chapter presents some of the international and national legislation covering the use of PFAS in P&B FCMs. Lists of PFAS used in paper and board (and in plastics) referred to below are mentioned in Chapter 2 and are given in the Appendices of this report.

2.1 European regulation for P&B

Concerning human health, food contact materials are regulated in the EU by framework regulation 1935/2004 on materials and articles intended to come into contact with food and any associated specific measures. Concerning environmental health, food contact materials are regulated in the European chemicals legislation, REACH (registration, evaluation, authorization and restriction of chemical substances). The main scope of this workshop is the regulation pursuant to regulation 1935/2004.

2.1.1 Human health

Food contact materials consisting of paper and board in the EU must comply with regulation 1935/2004 on materials and articles intended to come into contact with food. This regulation sets out the general requirements for all food contact materials and is therefore considered as the framework regulation.

Article 3 of this regulation requires that food contact materials be manufactured in compliance with good manufacturing practice so that, under normal and foreseeable conditions of use, they do not transfer their constituents to food in quantities which could:

- endanger human health
- bring about an unacceptable change in the composition of the food
- bring about a deterioration in the organoleptic characteristics there of.

[1] With input from the Danish Veterinary and Food Administration.

For the use of fluorinated chemicals in paper and board, point a) is particularly important. Producers and importers of paper and board must assess the risks of the fluorinated chemicals present in their paper and board food contact materials to ensure that these are not migrating to food in amounts that can endanger human health.

For five categories of FCMs, plastics (virgin and recycled), ceramics, active and intelligent packaging and regenerated cellulose, specific measures in support of regulation 1935/2004 are set out. These can include an exhaustive (positive) list of chemicals which can be used in the production of the FCMs and any possible restrictions concerning their content in the FCMs or their migration from the FCMs to food. EU-specific measures are based on risk assessments of substances or groups of substances performed by the European Food Safety Authority (EFSA). They are therefore considered a help in the production of FCMs and for the compliance work done in the supply chain, which ranges from suppliers and producers of raw materials to final FCMs. Currently there are no EU-specific measures for paper and board.

An overview of all chemicals used in European FCMs for which there are no harmonized specific measures (the so-called non-harmonized materials), was assembled by the European Food Safety Authority (EFSA) in 2011 in the ESCO report (EFSA, 2011).

2.1.2 Environmental health and non-food human exposure

REACH regulates the use of chemicals in FCMs only in the case of environmental health. REACH currently manages chemicals according to three categories of tonnage use, which specifies when and how companies must send their applications for evaluation by the European Chemicals Agency (ECHA).

As FCMs are already regulated in relation to human health by the framework regulation 1935/2004, FCMs are exempted from some of the requirements in REACH. This means that the authorization procedure does not apply to FCMs, unless the chemical is authorized due to environmental health concerns (article 56(5)(b) of the REACH regulation, 1907/2006) and the chemical safety report is not required to include an evaluation of human health risks (article 14(5)(a) of the REACH regulation, 1907/2006). However, there is no explicit exemption for the use in FCMs for restricted substances. So the REACH restriction for PFOA and related substances, proposed by Germany and Norway and entering into force on July 4, 2020, will include FCMs. The restriction limits PFOA and its salts to 25 ppb and one or a combination of PFOA related substances to 1000 ppb. The restriction will cover products produced in the EU as well as products imported to the EU.

2.2 Some national legislation for P&B

2.2.1 *German recommendations*

The German risk assessment institute, Bundesinstitut für Risikobewertung (BfR), has a database with recommendations for food contact materials, which the German Federal Ministry of Food and Agriculture refers to. These recommendations were published for the first time in 1958, but they are updated regularly, in part due to applications by industry for chemicals that they wish to use in food contact materials.

For paper and board, a general recommendation and two specific recommendations exist, which cover paper and board for baking purposes and cooking papers, hot filter papers and filter layers. These recommendations identify a list of fluorinated chemicals, which on the basis of human health risk assessments by BfR, can be used in paper and board for food contact, but with suggested restrictions in terms of maximum content in the paper. The latest edition of the German recommendations for paper and board is from July 2016 (Appendix 1).

Since it is a recommendation it does not have legal status, but it is often referred to in in-house documentation for FCMs consisting of paper and board. The BfR mainly provides the maximum allowed quantities in the material for which migration will be safe (Irvine and Cooper 2009) ("quantity in the material" (QM) value in units of % (w/w) of the material) or the maximum extractable amount ("quantity per area of the material" (QMA) value in units of $mg \cdot dm^{-2}$). Their test conditions are therefore extraction conditions.

2.2.2 *Other national regulations in EU member states*

The Netherlands has national regulations for food contact materials, which include specific regulations for paper and board. Similarly to the German recommendations, this includes a list of fluorinated chemicals which can be applied for paper and board for food contact, together with restrictions in terms of content in the material or migration. Also, the maximum allowed migration of fluorine from paper and board is 1 mg/kg food. The Dutch regulation recommends the use of similar food simulants as for plastics (Regulation 10/2011). Appendix 5 contains more information on the Dutch regulation.

Italy has national regulations for food contact materials which include a list of fluorinated chemicals that can be used as auxiliary and adjuvant substances, with specific restrictions in terms of content in the FCMs (Appendix 6).

Belgium has national legislation for food contact materials which includes restrictions for two fluorinated substances that can be applied for paper and board for food contact (Appendix 7).

2.2.3 US FDA

The US FDA regulates FCM by two separate positive lists of substances which companies can apply for being authorized for use in FCM of paper and board. These are the Code of Federal Regulations (CFR) list, which was used prior to 2000, and the Food Contact Notification (FCN) list, which was put in place after year 2000.

Substances on the CFR list have been evaluated, approved and considered safe to use, by any producer as long as they follow the guidelines by the US FDA. This is similar to the EU positive list of substances used in plastic FCM (Regulation 10/2011). In order to remove a substance from the CFR list, the US FDA must provide the evidence to reevaluate the substance. Alternatively external parties, such as civil society, can file a so-called food additive petition (FAP) for a reevaluation of the safety of the substances based on new scientific evidence. PFASs have been on the CFR list since the 1960s, but in January 2016 three so-called "perfluoroalkyl ethyl containing food-contact substances'[2], (FTOH derived PFAS being long chain precursors including SaM-PAPs and S-diPAPs) were removed from the list[3]. The substances were removed following a FAP (FAP 4B4809) by nine environmental and human health groups, since the FDA evaluation concluded that "*... that there is no longer a reasonable certainty of no harm for the intended use of the substance"*. The underlying concern is the biopersistence (i.e. bioaccumulation and persistence, analogous to the vPvB criteria used by ECHA) and reproductive and developmental toxicity of the class of long-chain PFAS. The three phased-out PFAS substances may no longer be applied in the US, but they can still be imported in finished FCM products. In addition, in April 2016 the company 3M voluntarily withdrew two PFAS[4] from the 21 CFR 176.170 based on the argument that their uses are abandoned[5].

Substances on the FCN list are approved for specific companies, producing them in a specified way, and it is the responsibility of the company to provide the risk assessment. In case new concerns arise about a substance, the US FDA can therefore ask the companies to provide further evidence that the product does not release harmful substances. This has led companies in 2012 to withdraw several fluoroacrylates, containing long-chain PFAAs from the FCN list:

[2] Diethanolamine salts of mono- and bis (1H,1H,2H,2H perfluoroalkyl) phosphates where the alkyl group is even-numbered in the range C8–C18 and the salts have a fluorine content of 52.4 percent to 54.4 percent as determined on a solids basis; 2. Pentanoic acid, 4,4-bis (gamma-omegaperfluoro-C8-20-alkyl)thio] derivatives, compounds with diethanolamine (CAS Reg. No. 71608–61–2); and 3. Perfluoroalkyl substituted phosphate ester acids, ammonium salts formed by the reaction of 2,2-bis[([gamma], [omega]-perfluoro C4-20 alkylthio) methyl]-1,3-propanediol, polyphosphoric acid and ammonium hydroxide.

[3] Federal Register /Vol. 81, No. 1 /Monday, January 4, 2016 /Rules and Regulations, pp 5-8. 21 CFR Part 176, Docket No. FDA–2015–F–0714, Indirect Food Additives: Paper and Paperboard Components

[4] Ammonium bis (N-ethyl-2-perfluoroalkylsulfonamido ethyl) phosphates, containing not more than 15 percent ammonium mono (N-ethyl-2-perfluoroalkylsulfonamido ethyl) phosphates, where the alkyl group is more than 95 percent C8 and the salts have a fluorine content of 50.2 percent to 52.8 percent as determined on a solids basis; and 2. Perfluoroalkyl acrylate copolymer (CAS Reg. No. 92265-81-1) containing 35 to 40 weight percent fluorine, produced by the copolymerization of ethanaminium, N,N,N-trimethyl-2-[(2-methyl-i -oxo-2-propenyl)-oxy] -,chloride; 2-propenoic acid, 2-methyl-,oxiranylmethyl ester; 2-propenoic acid, 2-ethoxyethyl ester; and 2-propenoic acid, 2[[(heptadecafluorooctyl) sulfonyl]methyl amino]ethyl ester.

[5] Federal Register/Vol. 81, No. 83/Friday, April 29, 2016/Proposed Rules, pp 25625-25627. 21 CFR Part 176, Docket No. FDA-2016-F-1153, Indirect Food Additives: Paper and Paperboard Components

(http://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/Notifications/ucm308462.htm).

The FDA currently considers there to be two different classes of fluorinated substances – those containing a continuous perfluorinated alkyl chain of 8 carbons or longer (C8), and those with a continuous perfluorinated alkyl chain of 6 carbons or shorter (C6). It is the opinion of FDA that there are unresolved safety issues with C8 perfluorinated materials and that until those safety issues are resolved there is no longer a reasonable certainty of no harm for the use of those substances. FDA does not have the same safety concerns for C6 perfluorinated materials, and FDA reviews those materials on a case-by-case basis through the Food Contact Notification (FCN) program.

In relation to migration, the US FDA regulations mainly have maximum allowed quantities in the material, as in the BfR recommendation. However, the US specifically mentions choice of migration conditions in relation to PFAS migration in their pre-notification guideline to the industry (US FDA 2010a), by advising the industry to contact the US-FDA for further guidance. It was the US FDA which first raised wider attention to the issue of PFAS migrating from food paper and board (Begley et al. 2005 and 2008).

2.3 Stockholm convention

The Stockholm convention on persistent organic pollutants is anchored under the United Nations Environment Programme (UNEP) and has been signed by 152 countries. Since 2009, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride have been listed in Annex B of the Stockholm Convention. This means that PFOS compounds are restricted to some defined uses under the Convention. These various so called acceptable purposes and specific exemptions are listed in Annex B in the Convention. Substances on this list are currently assessed on the basis of available scientific, technical, environmental and economic information, and will be evaluated if any of these acceptable purposes are necessary to maintain in the Convention if feasible alternatives are available on the market. The main aim of the legal process is to place PFOS and its related substances into annex A, which is equal to elimination. While PFOS and its derivatives are in Annex B, they are allowed to be used in FCMs, but will be prohibited if they enter Annex A. Other PFAS are currently under evaluation, such as PFHxS, and also PFCAs and their precursors, such as PFNA, PFDA, 8:2 monoPAPs, 8:2/8:2 diPAPs and 8:2 FTOH. These were evaluated by the Swedish based International Chemical Secretariat (ChemSec, http://www.chemsec.org/what-we-do/sin-list), using the same risk evaluation criteria as used by REACH and UNEP, and were therefore added to the SIN list (Substitute It Now) in October 2014. Substances on the SIN list are typically entering the UNEP Annex B "waiting list", if the evaluations are found to be valid. A key point for entering the Annex A list is that technical alternatives for PFAS can be found.

2.4 Chinese regulations

On 17 October 2016, China adopted a new regulation (GB 9685-2016) called "National Food Safety Standard – Standard for the Use of Additives in Food Contact Materials and Articles". This regulation also covers paper and board for food contact, and entered into force on 17 October 2017. The standard applies both to mainland China (regulated by the Ministry of Health of the People's Republic of China (MOH)) and to export out of China (regulated by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ)). The regulation has been assembled since 2013 and has sought inspiration in the European, Japanese and US regulations, also in relation to test conditions. In the preface to the regulation it is specifically mentioned that three fluorochemicals, including perfluoroacrylate copolymers used in the manufacturing of paper and board, have been removed compared to the previous standard (GB-9685-2008). This is in line with the developments in the US FDA regulations. The current GB 9685-2016 list now contains 19 fluorochemicals, three of which specifically mention use in paper and board, as shown in Appendix 8. Of the three, one is a polymer PFPE-type (marked in red), one contains a C6-perfluoro chain (i.e. a precursor of PFHpA, marked in blue), and one is PFOSA sizing agent (marked in green). In addition, the fluorochemicals used in inks, adhesives and in polymers may be present in paper and board multilayer materials. Overall, China therefore now has the most restricted list of authorized long chain fluorochemicals, compared to the US or Europe. In the next year or two, a second round of updates is expected to take place, which might further shorten the list. It would therefore be possible to seek some degree of harmonization between restrictions on fluorochemicals in European member states and in China. See Appendix 8.

2.5 Drinking water regulations

Drinking water limits for PFAS are currently under revision in many countries, in the EU and US, and in May 2015, new criteria (administrative limit values) were set for 12 PFAAs (PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA) in Danish drinking water at a sum of 0.1 µg/L (Miljøstyrelsen, 2015). As in countries which have had limits for some time, the limit values are decreasing, and comprising more PFASs, and typically PFAAs are being included in the sum values. A review of the limit values for PFAS in drinking water in 2011 is summarized by Stahl et al. (2011). For comparison, some of the existing and proposed limits relating to intake of PFAS via FCMs or drinking water are given in Table 3.

Table 3: Comparison of some limists for PFAS in FCMs and drinking water

Legal Proposition	Norwegian-German REACH restriction for PFOA Precursors in products / FCM (ECHA 2014)	German drinking water limit value for PFAA (Stahl 2011)	Limit value for PFOA in plastics (EC 10/2011)	Previous Danish actionvalue based on EFSA TDI values from 2008
Limit value	2 ppb (µg/kg FCM) for sum of PFOA and its precursors in the FCM	0,1 µg PFAA/L	10 µg PFOA/kg food	90 µg PFOS/kg food 9 µg PFOS/kg food
Corresponding limit in paper	2 ppb (µg/kg FCM) for the sum of PFOA and its precursors in the FCM	-	1 µg PFOA/ dm plastic	
Corresponding limit in food	0,2 µg PFOA eq/kg food	0,1 µg PFOA/kg food	10 µg PFOA/kg food	PFCA and its precursors: 90 µg PFOA eq/kg food PFCA and its precursors: 9 µg PFOS eq/kg food
Corresponding limit in TOF units			0,69 µg F / dm plastic	9 µg PFOA or 0,9 µg PFOS F / dm paper
Comments	PFOA and its precursors in the material		Only PFOA migrated to food or food simultants	PFOA and PFOS precursors in the food or the food simulant
Measuring method	Requires specific determination of single substances, e.g. by SPE-IC and GC-MS	Requires specific determination of PFAA, e.g. by SPE-LC-MS	Requires specific determination of single substances, e.g. by SPE-LC and GC-MS	Requires specific determination of PFOA and PFOS precursors in the migratet
LOD		PFAA < 0,001 µg/L	-	0,02-1 µg/l migrate (50% ethanol)
Can it deal with emerging and new PFAS?	Partly: Flourinated substances that degrade to PFOA	NO	Not relevant	Partly Fluorinated substances that degrade to PFOA/PFOS

3. Analysis of fluorochemicals in paper and board

Xenia Trier

Analysis of PFAS consists of a sample preparation part (in the material, in a food simulant, or in food), and detection of the compounds. This chapter describes the most common quantitative detection methods, being target and semi-target mass spectrometric methods and screening for total organic fluorine. Methods that are less commonly used will not be described here, such as 19F nuclear magnetic resonance (NMR), sliding spark, and Raman spectroscopy, since they are either too expensive or not sufficiently sensitive to be considered as options for compliance testing.

3.1 Detection

3.1.1 The situation in brief

To truly determine the sources and exposures of PFAS from paper and board to food and the environment would require standards for all produced PFAS and their impurities and degradation products. At present there is no overview of the identity of all those PFAS, and even fewer standards are available. The situation is not made easier by the emergence of new fluorochemicals, some of which are chemical mixtures such as oils and polymers (Trier et al. 2011a, Dimzon et al. 2016, Wang et al., 2014 a and b). This makes it difficult and expensive for public and commercial laboratories to provide updated methods which are capable of measuring the specific PFAS. In Denmark, no commercial laboratories currently offer analysis of the polyfluorinated PFAS precursors used in paper and board. The reason given is that the demand for specific analyses is too small, because there is no specific legislation and hence no limit values to test compliance for.

In Denmark and Sweden, commercial laboratories have target LC-MS methods for perfluorinated acids (PFAAs), for some PFOS derivatives, and for total organic fluorine (TOF). If limit values were set for PFAS in paper and board, the Danish commercial laboratories estimate that they would optimize the methods to check the limit. This would ideally require LODs ten times below the limit(s) and a collaborative test of the method, to ensure a high degree of certainty in the compliance testing.

In addition, several universities in the Nordic countries have both target and non-target LC and GC-MS methods covering anionic PFAS (e.g. PFAAs, PFOSA, FTS, and others) and neutral PFAS (e.g. FTOHs), but not covering cationic PFAS in methods for analysis of P&B.

Analysis of chemicals can be divided into 1) screenings, as *non or semi-target* analyses, typically used for exploratory research, and 2) specific analyses, called *target* analyses, typically used for confirmatory research. More details are given below about the difference between these types of analyses and their pros and cons.

3.1.2 Screenings

It is typical to screen for PFAS when it is not known whether or which PFAS are present in a sample. It is also common to screen for PFAS if standards are unavailable and no previous target methods have been made. If PFAS are present in a sample, the next step would be to determine their identity. Truly identifying "non-target" unknowns is a time-consuming and iterative process (Fitzpatrick et al. 2004, Ibáñez et al. 2009, Hogenboom et al. 2009). It involves sample preparation steps to fractionate samples, highly specialized equipment, such as high resolution mass spectrometry (HRMS) and nuclear magnetic resonance (NMR), data processing tools for calculating plausible elemental compositions, and synthesis of the suspected compound to verify a proposed structure. To limit the number of possible chemical structures, it is therefore advantageous prior to the chemical analyses to assemble as much information as possible about the chemicals which are likely to be present in the sample.

A first step in a non-target analysis is typically to screen for likely or suspected target contaminants (Pavlic et al. 2006, Ibáñez et al. 2009, Hogenboom et al. 2009) called "semi-target" analysis. The search is often done by setting the detector to look only at signals specific to the analyte of interest, such as the mass (*m/z* value) of the analyte. When a mass spectrometer (MS) is coupled to chromatography, so-called extracted ion chromatograms (EIC) can be made by displaying only the signal of the suspected *m/z* values. By identifying some of the peaks, the remaining number of unknown peaks can be reduced.

After identification, peaks can be quantified. If standards are unavailable, the PFAS can at best be semi-quantified. This is typically done by quantifying the PFAS using the calibration curve for a known and structurally similar PFAS compound, which can be termed as Quantitative Structure Concentration Relationship (QSCoR). This is similar to "read-across", used to assign the potency of a chemical in toxicology, and will similarly introduce uncertainty into the exposure assessment and hence the risk assessment.

Accurate mass spectrometry can also be used for simultaneous quantitative confirmatory analysis with exploratory screening (semi-target and non-target), which is the method used at the DTU National Food Institute in paper and blood matrices. Sufficiently high sensitivity was achieved by coupling on-line SPE to UHPLC-QTOF MS, resulting in LODs from 0.03–0.6 ng/mL (corresponding to approximately 0.01 to 0.2 ng/cm^2 paper).

3.1.3 *Screening for non-specific organofluorine compounds*

Several non-specific methods exist which can screen for just fluorine. These include sliding spark, droplet test, 19F NMR, Raman spectroscopy, and combustion of the total organofluorine followed by measurement of the fluoride by either an electrode or ion chromatography. However, only the latter (the Combustion Ion Chromatograph method) is sufficiently quantitative to be used as a confirmatory enforcement or compliance method for detection of the total amount of fluorine (TOF), and this method will be discussed below, for water and for FCMs.

In the TOF method, the organic fluorine is determined by subtraction of the inorganic fluoride (measured by ion chromatography in a liquid extract) from the total organic+inorganic fluoride (measured by ion chromatography after combustion (mineralization) of the sample (Miyake et al. 2007) and in rats (Yeung et al. 2009)). A drawback of this method is that if the inorganic fluoride >> organic fluorine (as is typically the case in groundwater and drinking water) , then the two large number are subtracted from each other, which results in a low precision in the determination of organic fluorine. To improve the method, Wagner et al. developed an adsorbable organic fluorine (AOF) method coupled to combustion ion chromatography (Wagner et al. 2013). The organofluorines and inorganic fluoride were extracted from the water by adsorption onto a solid sorbent (synthetic divinylbenzene-activated carbon: DVB-AC), followed by removal (displacement) of fluoride by NO3-. Subsequently, the total organic fluorine was determined by combustion ion chromatography. Some challenges still exist regarding the precision and accuracy of water analysis of TOF using the given method.

A Combustion Ion Chromatograph method, with fluoride subtraction, is currently being validated for paper and board matrices. The LOQ is expected to be a factor of 10 lower (LOQ: 0.01 µg F- absolute) in paper than for water, since the LOQ in water is mainly determined by the fluoride blank of the solid sorbent (activated carbon), which is not used in the paper analysis.

To transfer this to units of µg/kg food, the LOQ is determined:

- LOQ = 0.01 µg F-/cm2 = 1 µg F-/dm2 = 10 µg F-/10 dm2 = 10 µg F-/kg food

However, since the surface-volume ratio of the packaging can vary from approximately 6 to 100 dm2/kg food, the LOQ can vary accordingly from approximately 6 to 100µg F-/kg food. The limits can be lowered if more material is taken into use, and work is ongoing to reduce the LOD and LOQ.

The method is quite simple and the cost is rather low, which makes it suitable for compliance testing and enforcement. However, the method does not work on liquid extracts and/or migrates, since the combustion chambers are not suited for liquids. This part should be further developed and tested. An option could be to combine it using the AOF-F method, as this might be technically possible. Since this method measures all organofluorines in a sample, it makes it useful also to estimate total PFAS exposure.

3.1.4 *Specific determination of PFAS and groups of PFAA precursors (target analysis)*

In target analyses, the compound of interest is known, and a purely analytical reference compound (a "standard") is available. Target analyses are used in confirmatory research to study a well-defined question and to provide quantitative data which can be used as input for risk assessment. PFAS are typically quantified by methods coupling liquid or gas chromatography (LC or GC) to a mass spectrometric (MS) detector. The purpose of the chromatography is to separate the mix of PFAS compounds in a sample from each other, so they ideally arrive one at a time at the MS detector.

In the case of PFAS in food contact materials, the studies have mainly focused on the PFAAs (Kissa 2001), but their commercial applications are limited (US EPA 2002). Nevertheless, they have been studied for more than a decade, and have been found to be ubiquitous in the environment, biota, and humans (Giesy and Kannan 2001 and 2002, Houde et al. 2006, Lau et al. 2007, Olsen et al. 2009, Calafat et al. 2007, Kato et al. 2011). Pure analytical and isotopically-labelled standards can be bought for the PFAAs, and it is therefore possible to make target methods for them typically by LC-ESI-MSMS (D'eon and Mabury 2007, Lee et al, 2010), whereas the nonionic PFAS have been mostly analysed by gas chromatography (GC) MSMS methods.

However, for the commercial PFAS, only a few studies have investigated the types and measured the levels of PFAS in paper (Begley et al. 2005 and 2008, D'eon and Mabury 2007, D'eon et al. 2009, Lee et al. 2010, Trier et al. 2011a, b, c). Possibly due to the limited focus on testing the commercial PFAS, pure standards are not commercially available, which complicates method development. Instead, industrial blends must be used to make semi-quantitative methods (Begley et al. 2008), but even the industrial blends can be difficult to obtain for research purposes (Trier et al., 2011a).

3.2 Migration and testing of PFAS from paper to food and food simulants

3.2.1 *Transfer of PFAS from a physico-chemical point of view*

The levels of migration of PFAS's from FCMs into food vary with the amount, type and chain length of the substance, the type of food, the contact time and the temperature (Begley et al., 2008).

The migration of PFAS from paper and board is moreover a process which depends on:

- how easily the PFAS can be released from the paper
- if there is an (energetic) preference by substances to go into the food rather than to stay on/in the paper.

3.2.2 *Desorption of PFAS from paper surfaces*

The first step during migration of PFAS to food is the release of the PFAS from the paper surface of the food contact material. Whether the PFAS is adsorbed onto a paper surface or bloomed to the surface of a varnish used to coat the paper with, the release of PFAS can be understood in the same physical and chemical terms as the cleaning of a surface (Kissa 2001). Obviously, if the PFAS is not bound to the paper it more easily released. This is the case, for instance, for the residual impurities of PFAAs and FTOHs (non-intentionally added substances, NIAS), but also for certain types of physisorped fluorosurfactants.

The release of a substance, such as a PFAS, from a surface requires the surface to be wetted and the bonds between the substance and the surface to be broken. It is similar to washing dirt off our dishes with a detergent, or when sprinkler fluid cleans the windscreen of a car: the alcohol/detergent in the sprinkler fluid has a lower surface tension than the glass, and is therefore able to "wet" the surface, whereby the dirt is released into the sprinkler liquid. The process of releasing a substance from a surface is described in more detail in Kissa (2001) as the process of cleaning a surface. Liquids, which reduce the interfacial tension, such as surfactants and alcohols like isopropanol, methanol and ethanol, are good wetting agents, which makes them good cleaning agents.

Since water at room temperature has a high surface tension, it is not good at wetting fluor-coated paper. However, at higher temperatures the surface tension of water decreases, whereby water becomes better at releasing chemicals from surfaces. This has also been observed in studies, where increasing the percentage alcohol from 10% to 30% ethanol/water food simulants increased migration of PAPs at 100 °C (Begley et al 2008). In contrast, at room temperature, the migration to the food simulant 10% ethanol was negligible, but migration to 50% ethanol was significant and similar to 95% ethanol (Trier 2011a). This was also observed for butter where the migration of PAPs was negligible at 5 °C, whereas migration at 20 °C to more liquid butter was measurable (Barner, 2013). In relation to emulsified systems, Begley et al. (2005, 2008) showed how the migration from a PFAS coated paper was very minor to water or oil, but increased with the percentage of ethanol added to the water, or with emulsifier added to the oil. Weaker electrostatic and hydrophobic bonds (physical adsorption) which are reversible processes, can be broken by shifting the equilibria towards the solution. Ultrasound, which is used to dissolve crystals of chemicals, might also aid dissolution of physically bound PFAS. The properties of the paper are other relevant factors. Higher migration can occur from a surface which is porous or has cracks in it. Prolonged time in contact with an aqueous liquid will also make the paper material swell or even disintegrate. The more open the paper structure is, the faster the PFAS can migrate from it, particularly for PFAS residing inside the paper.

Overall, a combination of heating, moisture and/or the presence of emulsifiers such as alcohols or other food emulsifiers increase the migration (PERFOOD, 2013). This has been shown for ester-bound PFAS surfactants such as the PAPs (Barner 2013), which likely are bound to the cellulose fibres containing a lot of hydroxyl groups (Trier 2011), but can also be expected for fluoroacrylate ester bound coatings. The key point is that the PFAS is released by hydrolysis, which is sped up

by heating and if moisture or hydrolysing chemicals such as water or alcohols can get in between the paper and the coating. This in turn requires that the paper can be wetted.

However, to keep the analytes in solution, the equilibrium must be shifted toward the liquid phase. It is therefore useful to look at which phenomena favour dissolution of PFAS.

3.2.3 Migration of PFAS into foods

Based upon the previous discussion it seems likely that PFAS upon migration into foods will have a preference for surfaces, in particular of high energy, and for emulsified systems. This is supported by several studies. PFAS have a strong preference for binding to proteins (D'eon et al. 2010), and this is consistent with numerous studies which find that PFAS primarily are present in foods rich in proteins (especially liver, fish, and red meat). PFAS are also found in potatoes/French fries which are rich in starch (Tittlemier et al. 2007, Fromme et al. 2007), however, to a lesser extent than in meat. From a chemical point of view, starch contains a lot of OH groups, and in this respect starch resembles the polyalkoxylates (such as polyethylene glycols), which are common solvents for fluorochemicals. However, there might also be other reasons why PFAS are found in potatoes, e.g. if PFAS adjuvants are used in pesticides used specifically for potatoes, or some other processing chemical.

The migration characteristics of PFCAs and FTOHs of various chain lengths from paper and board into water and food simulant of different ethanol/water solutions (10:90, 30:70 and 50:50) were measured in a recent study by Yuan et al, 2016. The migration efficiencies for both FTOH and PFCA increased with a higher ethanol/water ratio, and short chain FTOHs and PFCAs were shown to have a larger migration from paper and board into water and 10% ethanol compared to long chain analogues (Yuan et al., 2016).

The influence of the surface area of the food on the PFAS migration has not yet been studied. However, in a study of the migration of semi-polar migrants from plastics, the migration increased when the food contained particulates, such as pulp in apple juice. Also in wastewater, PFAS preferentially bind to the sludge, where the adsorption of PFAS increases with increasing fluorinated chain length, i.e. with the PFAS hydrophobicity (Bossi et al. 2008).

In relation to emulsified systems, Begley et al. (2005, 2008) showed how the migration from a PFAS coated paper was very minor to water or oil, but increased with the percentage of ethanol added to the water, or with emulsifier added to the oil. The level of migration of PAPs and other PFAS into food increased significantly (50 times) compared to migration into fat without emulsifier, despite a brief contact time (Begley et al., 2008). In the case of butter (an emulsified food) the amount of migration (at 40 days, 4 °C) was always greater than the migration into oil (at 24 hours, 40 °C).

The size of the fluorine group also affects its hydrophobicity and solubility. A CF_3 side group is thus comparable in size to an isopropyl group, $CH(CH_2)_2$, which gives the *F*-chains a higher degree of hydrophobicity (Krafft and Riess 2009). The hydrophobicity

of perfluorinated chains is illustrated by the fact that CF_4 is 7 times less soluble in water than CH_4 (Kraftt and Riess 2009). In general, and in conclusion, phenomena such as entropy therefore play a proportionally larger role for fluorocarbons, since their enthalpy energy contribution (from binding) is rather low (Krafft and Riess, 2009).

In practice this has the very important implication that it is not the *fluorocarbon* part of a molecule that *binds to* molecules or receptors in proteins etc., because the fluorocarbon chain does not make bonds. Where the PFAS molecule will transfer to depends on the *system*, and the PFAS will go to the site with the lowest energy. This means that if the composition of the system or the physical state changes, then the PFAS might go elsewhere. The presence of other emulsifiers is such an example. This means that it is not enough to focus on the fluorocarbon chain—one must consider the whole molecule *and* the system it is in to understand the PFAS distribution in a given biological matrix. This is conceptually very different from other hydrocarbon molecules, and means that the toxicity of PFAS are less likely to be described by K_{ow} or QSAR (quantitative structure activity relationship), since these parameters focus on binding to receptors and do not deal with the surrounding system.

Another crucial point, is that what determines the transfer of *perfluorinated* PFAS is not necessarily true for *polyfluorinated* PFAS, containing hydrocarbons, or even perfluorinated PFAS containing other atoms such as oxygen (e.g. in perfluoropolyethers, PFPEs) or sulphur. Since the non-fluorinated parts of the molecule, and the dipole present in the junction between the hydrocarbon and the fluorocarbon chains, give the polyfluorinated molecules a capability to form weak bonds to other molecules, this dramatically changes their ability to partition (solubilize) into fat, for instance. This is supported by the observation that FTOHs partition somewhat into fats and into hydrocarbon solvents (Barner, 2013). Likewise, it can be expected that other polyfluorinated PFAS to some degree can partition into fatty tissues. It has hence been observed that Freon gasses used for anaesthetics, being fluoroethers, can insert themselves into the cell-membrane in lung tissue (Krafft and Riess, 2009).

When it comes to food, in conclusion, the solubility of PFAS in food (and in food simulants) is therefore likely related in a non-trivial manner to the food composition, the temperature (e.g. room temperature vs. microwave oven), the presence of salts and emulsifiers (hydrocarbon surfactants) in the food, the types and total concentration of PFAS in liquid foods, the total surface area, and the surface energy of the surfaces.

3.3 Migration vs. extraction from a compliance testing point of view

For plastics, the food simulants and test conditions have been established through large EU research projects in the 1980s, and led to harmonized guidelines for how to perform migration testing for specific substances, as described in the original technical directives, now included in the plastics regulation (EC 10/2011). In addition,

mathematical migration testing is capable of modelling migration from plastics to food and food simulants.

For paper, such a thorough correlation has not been established between migration to food and to food simulants. However, Begley et al. have done some comparisons (Begley et al., 2008). Since there are no EU guidelines for testing paper and board, the choice of migration conditions could be debated, and the lack of robustness. For example, performing single sided migration tests can be quite time consuming and prone to error. From both an enforcement and compliance perspective, it is more convenient to test the "extraction" of paper under more robust conditions and shorter times than migration typically requires (up to 30 days for long storage times). However, in the case of a non-compliance screening test, real migration testing with relevant food simulant(s) will be needed. From a risk assessment point of view, data on the migration of PFAS into food or food simulants is also needed in order to assess exposure. Current migration testing approaches for PFAS in paper and board used in Europe and in the US are reviewed below.

3.3.1 European guidelines for migration testing

For the time being, CoE recommends applying the test conditions for plastics to paper and board as well, but as described above, only the alcoholic simulants are suitable for PFAS from a physicochemical point of view. On 1 May 2011, the Plastics Directive (EC 2002) was fused with the technical directives (describing test conditions) to become Regulation EC 10/2011 (EC 2011), see Table 4. The regulation has, like the US-FDA regulation, more alcoholic simulants which better simulate PFAS migration. These are 10% ethanol (A, which replaces water), 20% ethanol (C), and 50% ethanol (D1, to be used for emulsified foods). With a material intended for fatty food contact, screening analysis using 95% ethanol as a fat simulant (D2) substitute can be used at test conditions of 2–6 hours at 60 °C (CEN 2002). For dry foods and at high temperatures, the solid sorbent, MPPO (also called Tenax) is recommended. This sorbent is good for trapping volatiles and simulating the direct contact with fatty foods, but it remains uncertain if this aromatic–hydroxide system will be good at simulating the migration of PFAS to an emulsified, protein rich food. The various combinations of test times and temperatures for plastic are given in Regulation 10/2011 (EC 2011). Table 4 gives an overview of the main food simulants used in the EU and by the US FDA.

Overall, at this stage, where analytical methods for food have not been developed for the larger di-alkylated and tri-alkylated PFAS, and on the basis of both the physicochemical behaviour of PFAS and the studies by Begley et al. (2005, 2008), it therefore seems reasonable to choose ethanolic food simulants or substitute food simulants for testing. These could be 95% ethanol for screening purposes, 50% ethanol for migration testing into emulsified foods, and 10–20% ethanol for the rest (Irvine and Cooper 2009, Irvine 2009). In a US study (Begley 2005, 2008), migration was low but observed for 10% ethanol at 100 °C for 15 minutes. For dry foods, it is unclear which simulant best simulates the migration of PFAS into foods.

In the four studies conducted by DTU Food, 20, 50 and 95% ethanol have been used for testing. As described above (in section 4.2.2 Desorption of PFAS from paper surfaces), 20% ethanol gave irreproducible responses, and since 50% and 95% ethanol performed similarly, 50% ethanol is currently being used as the food simulant for migration testing of PFAS from paper and board at DTU Food.

3.3.2 US FDA guidelines for migration testing

The US FDA regulations mainly have maximum allowed quantities in the material, as in the BfR recommendation. However, the US specifically mentions choice of migration conditions in relation to PFAS migration in their pre-notification guideline to the industry (US FDA 2010a), by advising industry to contact the US-FDA for further guidance. In EN 15519:2007 (CEN 2007) there is a choice of an organic solvent (isooctane or 95% ethanol) for 2 hours and 20 °C (short contact times), 24 hours at 20 °C (long contact times), or 2 hours at 60 °C (baking temperatures), and full immersion of cut paper. This method is used to test compliance with the BfR regulation on paper and board (BfR 2009). The US FDA allows the use of ethanol mixtures under pressure (using autoclaves), which allows them to reach the industrially relevant sterilizing conditions of 121 °C. The test conditions for microwave applications are typically set to 15 minutes and 100 °C for aqueous simulants.

Table 4: Food simulants and substitute fatty food simulants in Europe and the US used to test for migration from paper and board

Foods	EC 10/2011/CoE (5)	CEN/TC 172	BfR	US FDA
Aqueous	A: 10% ethanol	water- cold or hot	water- cold or hot	10% ethanol or water†
Acidic	B: 3% HAc	3% HAc		10% ethanol or 3% HAc†
Alcoholic	Up to 20%: C/20% ethanol Above 20%: D1/50% ethanol	-	-	Up to 10%: 10% ethanol Above 10%: 50% ethanol
Fatty Substitute fatty food simulants:	D2: Vegetable oil) 95% ethanol, isooctane	Vegetable oil 95% ethanol Isooctane Acetone Acetonitrile Diethylether	95% ethanol, Isooctane	Food oil, e.g. Corn, Miglyol 812 or HB307 oil 95% ethanol ‡ Oil+emulsifier ¤20–30% ethanol ¤
Emulsified	D1: 50% ethanol	-	-	*
Dry	E: MPPO	MPPO	MPPO	*

Note: HAc: Acetic acid, MPPO: Modified polyphenyleneoxide (Tenax). † can be used if it is a more severe simulant than 10% ethanol. ‡ the previously used n-heptane is not allowed any longer. ¤ these conditions were used in the testing of PFAS by the US FDA (Begley 2005 and 2008). * for a number of applications including fluorinated paper coatings, the industry should contact the US-FDA for advice on testing conditions.

4. Human exposure from P&B among other sources

Xenia Trier and Gitte Alsing Pedersen

Human exposure to PFAS can result from various sources such as food, beverages (including drinking water), inhalation and in-house dust contaminated by PFAS from different consumer products such as textiles and impregnation products (Strynar and Lindstrøm, 2008; Bjørklund et al., 2009; Ericson et al., 2008; EFSA, 2011).

4.1 Direct versus indirect sources

Several human exposure models have suggested that direct exposure to perfluorinated acids (PFAs), such as PFCAs or PFSAs in food from contamination by the environment, is the dominant source of human exposure to these substances, with fish and seafood as major contributors (EFSA, 2012; Fromme et al. 2007). Recent studies comparing the exposure models with concentrations in human sera suggest that environmental contamination of PFAs in food may not be the (only) major source of PFAs (D'eon and Mabury, 2011 a and b; Fromme et al., 2009). It is estimated that human exposure to PFAs can occur either: 1) via direct exposure to the PFA itself, which includes PFA emissions from the life-cycle of [i] PFA-based products that contain PFAs or their derivatives as major ingredients, and [ii] other products in which PFAs and/or PFA derivatives are present as impurities, or PFA exposure can occur from 2) indirect exposure which refers to the formation of PFAs from metabolic processes and the degradation of precursors such as PFOSA- and fluorotelomer-based substances in the environment and biota. Human exposure involves a combination of direct and indirect sources, but it is difficult to determine the relative importance of the two sources. However, from the given data it is estimated that indirect exposures can present a significant source of the observed human PFA exposure (D'eon and Malbury, 2011a)

4.2 Intake of PFAS from food and drinking water

Food is assumed to be the main source of human exposure to the specific substances of PFOS and PFOA and this is also suggested to be the case for other PFAS (Fromme et al. 2007; Tittlemier et al., 2007; Domingo et al., 2012). Most data on PFAS in food is on PFCA and PFSA, and only limited data has been published on non-PFCA and non-PFSA.

One of the main reasons is the analytical challenge in analysing the many different substances.

Fromme et al. (2009) assessed the overall exposure to PFASs in the general population in Western countries, taking into consideration all the potential exposure routes. Using a simplified model, the average (and high) level of total exposure in adults was estimated at 1.6 ng/kg b.w. per day (8.8 ng/kg b.w. per day) for PFOS and 2.9 ng/kg b.w. per day (12.6 ng/kg b.w. per day) for PFOA—values which are well below the existing tolerable levels (TDIs) of 150 ng/kg bw/day and 1500 ng/kg bw/day, respectively.

In another study, PFOS and PFOA were measured in a selection of food items from local origin in Belgium, in drinking water, in settled dust in homes and offices, and in human serum (Cornelis et al., 2012). The test results were complemented with data from a literature survey and the intake by children and adults from food, drinking-water, settled dust and soil, and air were calculated. Dietary exposure dominated overall intake. For adults, average dietary intake equalled 24.2 (P95 40.9) ng PFOS kg/bw/day and 6.1 (P95 9.6) ng PFOA/kg bw/day, whereas for children, the dietary intake was about 3 times higher. The estimated exposure is higher than in the above study by Fromme et al. (2009), and a comparison of reported levels of intakes by different studies shows that dietary estimates of exposure to PFOS and PFOA vary by 10 to 20 times between different countries (Cornelis et al., 2012). This variation could not be attributed to differences in food consumption. Cornelis et al. conclude that attention should go to further refinement of the dietary intake assessment for PFCs, addressing both analytical aspects in the determination of PFCs and the representativeness of the food basket.

The total intake of the sum of perfluorcaboxylates (PFCAs) and PFOS in Canadian food from 2004 was estimated to be 250 ng/day (Tittlemier et al., 2007). It was estimated to account for 61% of the total adult exposure (from food, water, dust, treated carpet and cloth) to these substances. Exposure assessment and comparison to TDI, by EFSA in 2012, focused on PFOS and PFOA, as the TDI values are established by EFSA for only these two substances. The analysis included 7,560 food samples collected from 2006–2012 in 13 European countries and the samples were analysed for 27 different PFAS. The chronic dietary exposure to PFOS and PFOA was well below the above TDIs in all age classes, and for both average and high consumers. For PFOS, the dietary exposure estimate in the adult population was < 3.5% of the TDI for average consumers and < 6.7% of the TDI in high consumers. For the same consumer groups, exposure to PFOA was < 0.3% and < 0.5% of the TDI, respectively. Exposure in toddlers was two to three times higher compared to adults.

The main contributors to dietary exposure to PFOS and PFOA have been found to be fish and other seafood, fruits and fruit products and meat and meat products, but high variation in contribution was observed across dietary studies and age classes, possibly reflecting differences in dietary patterns. Based on only very limited quantified data on other single PFASs in food, only a rough exposure estimated was made, arriving at the evaluation that they are expected to be in the low ng/kg b.w. per day range or

even lower. Since no TDIs are available for other specific PFAS, it was not possible to evaluate the human risk from dietary exposure to these substances (EFSA, 2012).

Drinking water is reported to be in the low ng/l range if there is no large point source of PFC for the water source (Fromme et al., 2009). In a Norwegian study of tap water from different Norwegian water works in the Oslo area, the level of PFOA was 0.65–2.5 ng/L whereas the other PFCAs were below 1 ng/L. However, drinking water may be a significant source of PFC (in particular PFOA) depending on the water source. In drinking water produced from surface water in contaminated areas, PFOA was the main compound found in a German study, at the level of 500–640 ng/L (Hölzer et al., 2008). This is in accordance with another German study reporting high levels of PFOA (519 ng/L) followed by PFHpA (23 ng/L) and PFHxA (22 ng/L) in public water supplies produced from river water with bank filtration or artificial recharge (Skutlarek et al., 2006). The phasing out of PFOS and PFOA has encouraged the production of novel PFAS with a tendency towards shorter-chained PFAS (C_4-C6 chemistry) and away from the C8-chemistry (MST, 2016). Whereas the short chain PFASs are less bioaccumulable in humans and biota (but may accumulate in plants), they are more difficult to remove from drinking water in conventional water treatment plants (Eschauzier et al. 2012b; Sun et al., 2016) which can add to an increase in human exposure to short chain PFAS.

In-house dust contaminated by PFAS from different consumer products (such as textiles and impregnation products) is supposed to also be another important pathway for human PFAS exposure (Strynar and Lindstrøm, 2008; D'Hollander et al., 2010; Fromme et al., 2009). Reported levels of PFAS in indoor dust (sum of perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonic acid (PFOS), perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) ranged from 0.2 to 336 ng/g (median 3.0 ng g/1) (D'Hollander et al, 2010). Levels in office dust were higher ($p < 0.01$) than in house dust with the sum of PFAS ranging between 2.2 and 647 ng/g (median 10 ng/g). In both house and office dust, PFOA, PFOS and PFHxA were detected most frequently and were the dominant compounds. Calculating the resulting human exposure through dust ingestion, toddlers seem to be the most exposed age group (D'Hollanders et al., 2010) and the contribution from dust in the US is suggested to be nearly as great as from food for this age group (Egeghy and Lorber, 2011). For working adults, the work environment makes a substantial contribution to PFAS exposure (D'Hollander et al, 2010).

4.3 PFAS in paper and board and migration into food

The use of PFAS in paper and board can add to the contamination of feed, food and drinking water via environmental contribution. A German study has shown that feed grown on farmland with paper mill sludge mixed into the "soil improver" did accumulate PFAS, and this was transferred to grazing cattle, to grain, and to pigs, hens, and their eggs after eating the contaminated feed (Numata et al. 2014).

Moreover, food contact materials are a potential source of direct PFAS contamination in packed food, and several different substances have been found in food contact materials, including PFCA, PFSA, FTOH, PTFE and PAPs. However, there are only a few reports on the influence of food contact materials on the level of PFAS in food. Begley et al. (2005) found that analysis of PTFE cookware showed residual amounts of PFOA in the polymer in the low µg/kg range, while PFOA was present in microwave popcorn bag paper at amounts as high as 300 µg/kg. When testing migration of PFOA from the popcorn bags into food oil (Miglyol) after microwaving, a low level of less than 1 µg/kg PFOA was reported (Begley et al., 2005). However, the migration of fluorotelomers from popcorn bags into popcorn oil was also tested, and a total migration of 3–4 mg/kg of fluorotelomers to food oil was detected, with a migration of 1.4 mg/kg before heating and 2.1 mg/kg as a result of the heating (Begley et al., 2005). The migration of fluorotelomers is a potential (indirect) source of human exposure to PFOA. It was concluded from this study that the largest potential source of migratable fluorochemicals in FCMs appears to be paper with the addition of fluorochemicals coatings and/or fluorine additives.

In two studies by D'eon and Mabury (2007, 2011) it was demonstrated that oral exposure of rats to 8:2 mono or diPAPS resulted in increased PFOA blood levels (D'eon and Mabury, 2007; D'eon and Mabury, 2011). High levels of diPAPS up to 600–9,000 µg/g paper were reported in a Danish study of Danish, Swedish and Canadian FCM paper and board (Trier, 2011). This level was found to be in agreement with information given by the producers of paper and board that a total amount of fluorochemicals up to 4% (dry weight) of the paper mass can be used when mixed into the pulp (Trier 2011). Other samples had lower levels of 1–100 µg diPAPs/g paper and it was hypothesised that this could be related to a fluorine containing surface coating of the paper and board (Trier 2011).

Target analysis of PAP migration from Swedish packaging materials into food was tested for 14 food packaging materials randomly selected in a local supermarket and a fast food restaurant (Gebbink et al., 2013). The results showed the presence of mono-, di-, and/or triPAPs in all of the tested food packaging. Of a total of nine different diPAPs identified, the substances of 6:2/6:2 and 6:2/8:2 diPAPs were the dominant compounds. DiPAP concentrations in the food samples ranged from 0.9 to 36 pg/g, which was comparable to individual PFCA concentrations in the same samples.

In the packaged food, DiPAPs were detected in all samples (except one), whereas monoPAPs and triPAPs were not detected in any of them (Gebbink et al., 2013). Also, in food the 6:2/6:2 and 6:2/8:2 diPAP dominated the pattern. Concentrations of 6:2/6:2 diPAP in the food samples ranged from 0.9 to 13 pg/g, with the highest concentration found in prepared popcorn. The level of PAPs in the packaged food is believed to be due to both migration from food packaging materials and contamination from other sources in the production process. As degradation of PAPs may lead to the formation of PFCAs with varying chain lengths, the author concluded that consumption of food packaged in PAP-containing materials is also a potential indirect source of human exposure to PFCAs (Gebbink et al., 2013).

In Germany, 28 samples of frozen packaged French fries were analysed, with a migration of PFOA and PFOS below 1 µg/kg in the frozen French fries (Stahl 2007). Also perfluoroalkyl sulfates (PFSA's) like N-EtFOSA (N-ethyl perfluorooctane sulfonamide), N,N-Et2FOSA (N,N-diethyl perfluorooctane sulfonamide), N-MeFOSA (N-methyl perfluorooctane sulfonamide), and PFOSA can be used in grease and water repellent coatings in food packaging. Food can thereby become contaminated by these substances, contributing to human body burdens of PFOS by degradation of the mentioned precursors (Fromme et al., 2009; Tittlemier et al., 2006). The concentration of FOSAs in certain foods has decreased in recent years due to a cease in the production of perfluorooctylsulfonyl substances (Fromme et al., 2009).

Migration of Perfluorooctane sulfonamides (PFOSAs) was analysed in various Canadian foods. The authors (Tittlemier et al., 2006) assumed that the dietary exposure to FOSAs occurs mainly from food (such as French fries and pizza) packaged in paper treated with perfluoroalkyl coatings. According to Fromme et al (2009), the level of FOSAs in food has decreased as the use of these substances has been reduced.

In 2011, various samples (n= 84) of paper and board food packaging materials from the Danish market were analysed by total immersion of the samples into 50% ethanol (the simulator for dairy food according to EU Regulation 10/2011 on plastic FCMs). Various PFAS were found in 35 of the samples, including fluorotelomer alcohols in various types of packaging materials such as coffee bags, popcorn bags, paper and board for take away food, and cakes, and PFCA in popcorn bags (DFVF, 2011). For some of the PFAS, positive samples of migration into food or food simulants were further tested. The reported low levels of migration were in the range of < LOD -0.2 µg PFOA equivalents/kg food (DFVF, 2011). Begley et al. (2008) found that high temperatures and emulsified fats can significantly increase the extent of migration of PAPs and other PFAS into food (Begley et al., 2008), as given in chapter 4.

In the EU PERFOOD project (2010–2014), screening of fluorinated substances in paper and board FCMs was performed. The study found that baking papers, sandwich papers and butter wraps have the highest share of fluorine containing FCMs. From specific analysis, PAPs, S-PAPs and PTFE were detected in these kinds of FCMs, and FTOH was detected in almost every fluorine positive FCM sample (PERFOOD, 2013). Migration from the FCMs into food (including butter and cheese) and into Tenax was also tested. Storage of butter in packaging coated with a fluorinated polymer increased the levels of PFAA and particularly FTOH in the butter (Still et al., 2013), and it was found that the migration decreases with chain length. Baking paper and butter wraps were found to pose a high potential for migration of PFAS (including PFAS precursors such as FTOHs) into food, and surface-treated sandwich paper was estimated as an important source of exposure to PAPs from food. The migration rates of PAPs into emulsified and fatty foods like butter and cheese increased considerably compared to dry foods and Tenax, respectively. In the case of longer contact times and higher storage temperatures, an accelerated degradation of diPAPs to monoPAPs and FTOH was monitored, in addition to increased migration rates for PAP. Due to the degradation of diPAPs, the migration of FTOH into food increased as a function of time.

In a recent study, FTOHs were detected in 78% of P&B food packaging materials from China, with the highest median concentration of total PFAS detected in paper tableware (119 ng/g), followed by microwave popcorn bags (112 ng/g) (Yuan et al., 2016). Of the different substances, 10:2 FTOH was the FTOH detected in most samples from China, followed by 12:2 FTOH, 8:2 FTOH, 14:2 FTOH, 16:2 FTOH, 6:2 FTOH, and 18:2 FTOH. For comparison, in paper FCMs from the United States, 6:2 FTOH was the most frequently found substance and detected at the highest concentration among the different FTOHs analysed. Migration of FTOHs from the materials into different food simulants (water, 10%, 30% and 50% ethanol and oil) were tested, showing that migration efficiencies increased with decreasing carbon chain lengths of FTOHs and PFCAs. The migration was moreover found to increase with higher levels of ethanol, whereas migration into oil and in particular into water was low.

The above study shows a shift from long chain FTOHs to short chain substances (6:2 FTOH) in US food contact materials, whereas long-chain FTOHs were still more common in samples from China (Yuan et al., 2016). In recent years, there has been some shift away from fluorotelomer surfactants towards per- and polyfluorinated polymers, such as per- and polyfluorinated polyethers (PFPEs) (Dimzon et al., 2016). On the European market, this shift from telomeric PFCs to PFPE coatings is reported for popcorn bags and in fast-food packaging (NMKT, 2013). In 2009, analysis of samples taken from Denmark, Sweden and Canada found PFPEs in 7 of 50 samples by measurement using 19F NMR (Trier, 2011). In the US, nine out of 11 PFAS approved and registered by the FDA since 2008 are polymers that utilize 6:2 fluorotelomer substances (Schaider et al., 2017).

Due to the many different substances (including different usage patterns in different parts of the world) and their various degradation and metabolism products, it is difficult to properly estimate the human exposure to PFAS from different sources, including FCMs. EFSA concluded in 2012 that for a better exposure assessment of PFAS from food, more data and better analytical methods for analysis of PFAS are needed.

4.4 Human biomonitoring

In 2013, a Nordic report assembled data on human biomonitoring data in the Nordic countries (Norden, 2013). The conclusions in this report are given below.

In the Faroe Islands, data for 7 and 14-year-old children indicate a decreasing trend for PFOA during 1993–2003 (Posner et al., 2013). Nøst et al (2014) studied the temporal trends for exposure to PFAAs from 1979 to 2007 in males from Northern Norway. In five repeated measurements of PFAAs in human serum, they found that PFOA and PFOS concentrations peaked during 1994–2001 and 2001, respectively. However, PFNA, PFDA and PFUnDA increased throughout 1979 to 2007. Studies from other countries support these observations (Kato et al. 2011). In most studies, PFOA, PFNA, PFDA, PFUnDA and PFHpA have been detected in human blood, whereas PFHxA, PFDoDA, PFTrDA, PFTeDA have been below detection limits. In general, the blood levels are higher in males than in females.

FTOHs have been identified to be metabolized to PFOA and are thus a source of PFCAs, and it is hypothesized that fluorotelomere precursors or residuals (from fluorotelomer-based commercial products) can be an indirect source of PFOA, together with exposure to PFNA and PFDA, and explain the continued exposure to these substances without similar exposure to PFOS (Vestergren et al. ,2008; Wang et al¸ 2013; D'eon and Mabury, 2011). Further research is needed to determine whether the constant or slowly increasing concentrations of long-chain PFCAs in human serum are primarily a consequence of ongoing exposure to telomere-based precursors.

Intake of fish, shellfish, and whale were in some studies identified as determinants of PFAS serum concentrations. However, other factors, such as consumer products and indoor air (e.g. house dust) were also found to contribute to PFAS exposure. In general, comparable levels were observed for the Nordic countries, although the newest and lowest levels were found for Sweden and Norway.

In cord blood, mainly PFOA, and to some extent PFNA and PFDA, were detected, but the concentrations are usually lower than concentrations observed in maternal serum or plasma, although the maternal and cord blood data are highly correlated. Detection of PFCAs in cord blood means that some of the compounds can cross the placental barrier, and the foetus is prenatally exposed to these compounds. PFCAs with longer chains are transferred less efficiently to the foetus than those with shorter chains. Of PFCAs, only PFOA was detected in breast milk from women in Nordic countries, and the concentrations in milk are 3–4% of what is found in the corresponding serum concentrations (Haug et al., 2011). For comparison, in China, PFNA, PFDA and PFUnDA, in addition to PFOA, were also detected in some samples. Monitoring studies of PFCAs in amniotic fluids are scarce, but a Danish study detected PFOA and PFNA in amniotic fluids at concentrations 10–20 times lower than in maternal blood.

4.5 Challenges and data gaps for exposure to fluorochemicals from paper and board FCMs

A Nordic survey shows (Norden, 2013) that there are significant gaps in our knowledge of most fluorinated substances. This applies to knowledge of the quantities produced in the world, how much they are used in the Nordic countries, the precise chemical composition of fluorinated substances in commercial products including FCMs, how toxic they are, and what mechanisms make them toxic.

Only limited data has been published on non-PFCA and non-PFSA in food. One reason for this is the analytical challenge in analysing these substances, and adequate and good performance analytical methods are therefore a great need in this field.

Food contact materials may be a significant source of PFC contamination of food, and several different PFCs have been found in food contact materials, including PFCA, PFSA, FTOH and PAPs.

Moreover, new substances are currently being introduced into the market. ,Improvements to good performance and sensitive analytical methods (including

identification and quantification) aimed at identifying and quantifying these many different substances in FCMs and estimating migration are greatly needed in order to perform exposure assessment in this area.

Data to perform human risk assessment for fluorinated substances in paper and board is needed. This includes:

1. More data on migration from food contact materials into food of PFCs and especially of non-PFCA and non-PFSA is needed, to estimate the human exposure to PFCs from food contact materials. This should include monitoring the trends in usage of and exposure to PFC substances.

2.Toxicological evaluations of the specific substances relevant to exposure.

5. Human health effects

Camilla Taxvig and Anna Kjerstine Rosenmai

Perfluorinated compounds (PFAS) have emerged as important food contaminants. However, though the toxicological information is extensive for PFAS like PFOS and PFOA, and more limited for other perfluoroalkyl substances, the polyfluoroalkyl substances, such as FTOHs and other precursor compounds used in FCMs of paper and board, are poorly characterized for toxicological effects.

Prompted by the toxicity findings in animal models, countless epidemiological investigations in the general population have been launched in recent years. As great species and gender differences in the kinetics of PFAS exist, it is a challenge to extrapolate from animal to human data, and we will therefore focus on human data in this section.

The main evidence on adverse effects in humans comes from observational studies of occupational cohorts and community studies of subjects exposed either at background levels or through contaminated drinking water. However, new evidence is emerging, as a result of the "C8 Health Project" launched in 2005 to investigate the potential health effects of exposure to PFOA from drinking water in the Mid-Ohio Valley areas, where data on approximately 70,000 exposed Ohio and West Virginia residents provided information on drinking water intake, serum-PFOA concentrations, and a variety of possible clinical outcomes (C8 Health Project. 2009; Frisbee et al. 2009). Additional evidence on associations between PFAS exposure and disease parameters in the general population comes from the NHANES database (Calafat et al 2007).

A selection of the current epidemiological data is briefly described below, citing some of the most well described effects or endpoints.

5.1 Cancer

The US Environmental Protection Agency (EPA) draft risk assessment of PFOA concluded in 2005 that the evidence was suggestive of a cancer risk in humans, but peer review recommended that PFOA be considered "carcinogenic to humans" (US EPA, 2006). This conclusion is supported by the recent C8 Health Project results, which found a significant positive exposure-response relationship between PFOA and kidney cancer. A population-based case-control analysis supports the association between PFOA exposure and both kidney and testicular cancer, and suggests an association with prostate and ovarian cancer and non-Hodgkin lymphoma. For PFOS, the evidence of carcinogenicity is less extensive and less conclusive.

5.2 Reproductive and developmental toxicity

The reproductive and developmental effects of PFOS and PFOA have by far attracted the most attention. Weak associations between PFOA and PFOS exposure and reduced fertility in humans have been observed (Fei et al., 2009; Whitworth et al., 2012). A few human studies have also shown positive but weak associations between PFOA or PFOS exposure and preeclampsia, early menopause, delayed puberty onset, and semen quality, while other studies have shown no association with some of these reproductive parameters (Fei et al., 2009; Stein et al., 2009; Knox et al., 2011; Lopez-Espinosa et al. 2011; Joensen et al. 2009; Raymer et al. 2012; Louis et al. 2013). However, a recent prospective study shows an association between *in utero* exposure to PFOA and semen quality and reproductive hormones in male offspring 20 years later. PFOA was associated with lower total sperm count and a lower adjusted sperm concentration, and PFOA was also associated with higher adjusted levels of luteinizing hormone (LH) and follicle stimulating hormone (FSH), indicating that *in utero* exposure to PFOA may be contributing to reduced semen quality in adult men (Vested et al., 2013). Many of these effects are most probably induced by hormonal changes.

The relationship between maternal (measured during pregnancy or in cord blood) PFAS exposures, i.e. PFOS, PFOA, PFNA and PFHxS, and indices of foetal growth/development, including birth weight, birth length, ponderal index, gestational age, and pre-term birth, have been conflicting. Some have shown increased levels to be inversely related (Andersen et al., 2010; Apelberg et al., 2007; Fei et al., 2007; Wu et al., 2012; Darrow et al., 2013, Maisonet et al., 2012; Wang et al, 2011), whereas others have reported no effect or an opposite association (Fei et al., 2008b, Hamm et al., 2010; Olsen et al., 2009).

Studies investigating the association between age at menopause and PFNA or PFHxS exposure using the NHANES data found a monotonic association, and a similar association was also observed for the rate of hysterectomy (Taylor et al., 2013).

5.3 Metabolism and thyroid function

Numerous studies have looked at various clinical indices. Some studies have reported effects of PFAS exposure on thyroid, liver, glucose and lipid metabolism. Although there are some inconsistencies between the studies, exposure to PFAS, especially PFOA and PFOS, overall seems to be associated with thyroid disease, although there also seems to be some differences concerning effects in men and women (Melzer et al., 2010; Knox et al. 2011; Olsen et al., 1998; Olsen et al., 2003; Olsen et al., 2012; Gallo et al., 2012).

Thyroid function regulates a wide array of metabolic parameters, such as lipoprotein metabolism, and thyroid dysfunction can thus have an important effect on lipid profile and may influence the overall risk for cardiovascular disease. Current studies suggested a probable link between exposures to PFAS e.g. PFOA, PFOS, and PFHxS, and diagnosed high cholesterol (hypercholesterolemia). These observations

may be related to thyroid hormone disruption, as cholesterol levels may increase when TSH levels are high or T_4 levels are low, a typical situation in patients with hypothyroidism (Nelson et al., 2010; Kerger et al., 2011; Steenland et al., 2009; Frisbee et al., 2010; Fisher et al., 2013).

In addition, results from a number of exploratory cross-sectional studies analysing NHANES data suggested that serum perfluoroalkyl acids (PFAAs) are associated with altered glucose homeostasis, indicators of metabolic syndrome, and elevated liver enzymes (particularly in obese subjects).

Lin et al. (2009) reported that increased PFNA concentrations in adolescents in NHANES were associated with hyperglycaemia, decreased blood insulin and β-cell function, and higher blood glucose above the metabolic syndrome definition, but with a low prevalence of metabolic syndrome and high-density lipoprotein cholesterol. Similarly, in an analysis of data collected as part of NHANES, increased PFOS serum levels were associated with increased serum insulin, insulin resistance status and β-cell function in adults, and were correlated with high density lipoprotein-cholesterol (Lin et al., 2009a and 2009b). However, in another study by the same authors involving young individuals with hypertension (Lin et al., 2011), no relationship between exposure and metabolic syndrome (glucose homeostasis, adiponectin levels, lipid profile or inflammatory biomarkers) was observed. When the data was adjusted for confounders such as age, gender, lifestyle and various other blood parameters, the authors did, nevertheless, observe a dose-response trend with adiponectin levels (Lin et al., 2011). However, Fisher et al. (2013), in an analysis of data from the Canadian Health Measures, reported no association between serum PFOS levels and plasma lipids or metabolic syndrome, when adjusted for age, gender, BMI, alcohol, and smoking, and Wang et al. (2012) also reported no association between PFOS exposure and HDL in workers at a fluorochemical plant and nearby residents (Fisher et al., 2013; Wang et al., 2012).

A study on diabetics (NHANES samples) reported that those on non-thiazolidinedione medication had slightly raised serum PFHxS levels, compared to those on thiazolidinedione medication, and those individuals receiving no medication had a significantly reduced risk (Power et al., 2013).

5.4 ADHD

A few studies have also reported an increased odds ratio of attention deficit hyperactivity disorder (ADHD) with higher PFHxS or PFOS exposure levels (Hoffman et al., 2010; Stein and Savitz, 2011).

5.5 Immune function-related diseases

A study by Dong et al. (2013) measured serum concentrations of 11 PFAS (PFOS, PFOA, PFBS, PFDA, PFDoA, PFHpA, PFHxA, PFHxS, PFNA, PETA, and PFTeDA) and found serum concentrations of 9 out of 11 measured PFAS to be significantly higher in children

with asthma than in those without. In addition, for most of the PFAS, significant trends were also seen for 2 or all 3 measured immunological biomarkers (IgE, absolute eosinophilic count (AEC), eosinophilic cationic protein (ECP)), and among asthmatic children, positive trends for associations with asthma severity scores were significant for PFOS, PFDA, PFDoA, and PFTA (Dong et al.,2013).

For PFOS, Uhl et al. (2013) reported from NHANES that the OR for osteoarthritis in the highest exposed group was significantly greater than that in the lowest, although the association was only observed for women. In a previous study by Innes et al. (2011) from the C8 Health Project, it was reported that the risk of osteoarthritis in a US population residing in areas with drinking water contaminated with PFAS (PFNA, PFOA, PFHxS, and PFOS) was significantly inversely associated with exposure levels.

Finally, potential immunotoxicity effects of PFOA and PFOS have been demonstrated in the form of an immune suppressing effect associated with exposure to PFAS. This was indicated by recent data on vaccine antibody responses in children. When childhood vaccination responses were used as a clinically relevant outcome, PFAS concentrations in maternal pregnancy serum showed a strong negative correlation with vaccine antibody concentrations in children at 5 years of age. While maternal PFOS and PFOA concentrations were not associated with hospitalization rates for infectious disease in their children, one study has shown increased rates of common infections (Grandjean et al. 2012).

6. Risk assessment considerations

Camilla Taxvig

A vast number of fluorochemicals are used in FCMs, some of which will be degraded to PFCAs and to PFSAs. However, no overview of the currently used FCMs containing PFAS or the composition or concentrations of PFAS in technical mixtures intended for use in FCMs exists. We also lack exploratory data for the identities, compositions, and concentrations of PFAS in technical mixtures used for FCMs. This hampers the development of confirmatory analysis of human exposure specifically from FCMs that is needed as input for quantitative risk assessment.

Nor do we know much about the extent of migration of PFAS to food items (as given in chapter 5). The present human exposure to PFAS caused by migration from FCMs is therefore unknown, and as we probably will not have this information in the near future, it will be challenging to risk assess specifically PFAS from FCMs.

Concerning toxicological knowledge about the PFAS used in FCMs there is a similar data gap, especially when it comes to the precursors used in FCMs, such as PAPs. Specific risk assessment of PFAS in FCMs is therefore a great challenge, but may—in light of the recent PFOA risk assessment (REACH restriction proposal by Norway and Germany, 2014)—be based on the uncertainty principle, as there should be a great incentive to reduce human PFAS exposure. A relevant question is whether total human exposure to these very persistent chemicals is acceptable, given that we cannot get rid of them if clear evidence of human health problems arises.

6.1 Application of a DNEL-derived approach for estimating risks of PFOA

In October 2014, Germany and Norway submitted a proposal for a restriction on PFOA, PFOA salts and PFOA-related products to ECHA (ECHA, 2014). The report covers a thorough evaluation of toxicity information on PFOA and introduces an approach based on DNEL (Derived No Effect Levels) and internal exposure levels as the basis for risk characterization. The results are shown in the tables below for adults and children, respectively.

Table 5: Risk characterization of PFOA for adults

General population adults		PFOA (ng/mL)		PFOA (ng/mL)	RCR	
Reference for DNEL estimation		Internal serum values		DNEL		
		Mean	High		Mean	High
Lau, 2006	Reduced mice pup weight	3.5	21	209	0.02	0.10
Abbot, 2007	Reduced neonatal survival in mice	3.5	21	277	0.01	0.08
Macon, 2011	Delayed mammary gland development	3.5	21	2	1.8	10.5
Steenland, 2009	Increased cholesterol and LDL in humans	3.5	21	0.73	4.8	28.8
Fei, 2007	Reduced birth weight in human offspring	3.5	21	0.3	11.7	70

Note: Table adopted from REACH restriction proposal by NO & GE, 2014. RCR: Risk Characterization Ratio. DNEL: Derived No Effect Level.

Table 6: Risk characterization of PFOA for children (according to REACH restriction proposal by NO & GE, 2014 as well as the Grandjean study)

General population children		PFOA (ng/mL)		PFOA (ng/mL)	RCR	
Reference for DNEL estimation		Internal serum values		DNEL		
		Mean	High		Mean	High
Lau, 2006	Reduced mice pup weight	6.4	108	209	0.03	0.51
Abbot, 2007	Reduced neonatal survival in mice	6.4	108	277	0.02	0.39
Macon, 2011	Delayed mammary gland development	6.4	108	2	3.2	54
Steenland, 2009	Increased cholesterol and LDL in humans	6.4	108	0.73	8.8	148
Grandjean (2013)	Reduced immune response in children	6.4	108	BMDL5/UF* 0.1	64	1080

Note: *) Benchmark Dose modelling (BMDL) divided by a UF of 10 to take intra-species differences into account

The conclusion from the above risk characterization is that there are clear indications that the most exposed individuals among the general population are not protected from the hazardous effects of PFOA. The current PFOA exposure is estimated to be 2–70 times higher than the maximum warranted exposure levels in adults and 3–1,080 times in children. As humans are exposed to several other PFAS apart from PFOA-related compounds, mixture effects should be taken into consideration, which will not make the scenario better. In general, the human studies resulted in lower DNELs than the rodent studies. The calculation based on immunotoxicity in children results in a reference dose that is 7 times lower than that based on hypercholesterolemia in humans.

6.2 Future perspectives

Based on the current available data, there is evidence for a PFAS-induced risk to human health amongst the people with the highest exposure. The new evidence for adverse effects on human health has not been taken into account in the evaluation of the Tolerable Daily Intake (TDI) for PFOA and PFOS from 2008 set by EFSA, and there is therefore a need for a re-evaluation of PFOA and PFOS, and a revision of the acceptable

intake. Such an EFSA evaluation is currently in progress with the aim of delivering two opinions 1) one on PFOS and PFOA by the end of 2017 and 2) one on other perfluoroalkylated substances in 2018 (EFSA, 2015 a and b). In a recent risk assessment of PFOA by US-EPA (US-EPA, 2014), 0.02 µg/kg bw/day was selected as the Reference Dose (RfD) for PFOA, based on the consistency of the response and with recognition of the use of liver weight as a common denominator for loss of homeostasis and protection against co-occurring adverse effects. This value should be compared to the Tolerable Daily Intake (TDI) derived from the EFSA risk assessment of 1.5 µg/kg bw/day. Similarly, for PFOS a RfD of 0.03 µg/kg bw/day was selected by US-EPA based on the consistency of the response and with recognition of the use of developmental toxicity and liver weight as the most sensitive endpoints for protection against co-occurring adverse effects. This value should be compared to the TDI derived from the EFSA risk assessment of 0.15 µg/kg bw/day. Thus, the US-EPA risk assessment recommends lower TDIs compared to the present European risk assessment.

Table 7: Comparison of the present EFSA TDI with US-EPA reference dose (RfD) for PFOS and PFOA

	EFSA 2008 TDI	US EPA 2014 RfD
PFOS	150 ng/kg bw/day	0.03 µg/kg bw / day 30 ng/kg bw/day
PFOA	1500 ng/kg bw /day	0.02 µg/kg bw / day 20 ng/kg bw/day

One of the current challenges is how to bridge data gaps for short-chained PFAS, acrylates and ethers, which are the compounds replacing the long-chained PCFs. A suggestion for how to bridge these gaps could be by the use of quantitative structure activity relationship ((Q)SAR) modelling, computational systems biology, and physiologically-based kinetic (PBK) modelling, as well as *in vitro* profiling of PFAS. The latter includes the evaluation and interpretation of available ToxCast™ data that comprise comprehensive mechanistic data for a subset of PFAS. By applying these computational and *in vitro* tools, it may be possible in the future to estimate the potential hazards of this large group of PFAS.

7. Risk management options for fluorinated chemicals in paper and board FCMs

Xenia Trier[6]

The focus of the workshop on fluorinated chemicals in paper and board for food contact was to gather as much information as possible concerning considerations for the available options for risk management, which will be detailed later in this chapter.

7.1 Considerations

Some general thoughts on risk management measures for the fluorinated chemicals in paper and board provided a starting point for the workshop program, and initially the following points were identified as important:

- Human health
- Risk assessments and availability of toxicological information
- Availability of analytical methods including their performance measures, e.g. robustness and limits of detection
- Availability of feasible and safe alternatives
- Economic consequences for industry
- Enforcement options

7.1.1 The responsibility of the FCM operators

The main responsibility for ensuring the safety of FCMs lies with the producer or importer of the FCMs. Considerations of the pros and cons of using fluorinated coatings or non-fluorinated alternatives depend on whether the business operator is a manufacturer, converter, importer, or food company.

For the *paper manufacturing businesses*, the use of alternatives to fluorinated chemicals depends on the availability of raw materials, their price, their functionality in

[6] With input from the Danish Veterinary and Food Administration.

the end product (e.g. their ability to repel fat and water over time and at high temperatures), their machinability, whether longer time or higher temperatures are required to produce the paper, and their compatibility with the other ingredients in the paper material. An example of an extra cost is greaseproof paper, which requires longer time and more energy to dry the finely ground paper fibres, which soak more water due to the grinding and delamination of the fibres. Higher costs might also be associated with the more pure raw material being virgin cellulose, which is needed for fluorine free paper, rather than recycled paper. However, other expenses might be lowered, for instance the cost of buying coatings. Also, the lower costs of protecting and educating workers in handling harmful chemicals, and disposing of chemical waste can cause a significant reduction in the costs of the production company, as has been documented in the US with substitution initiatives (EEA, 2013). If there are extra costs associated with the production of the non-fluorinated alternatives, this might increase the price of the product, which can be acceptable if there is a demand for such material, e.g. due to pressure from consumers and first-moving retailers or compliance with specific legislation. According to the guidance for the Declaration of Compliance (DoC), it is the manufacturer, converter and importer that provide the analysis or specific information that must follow the FCMs to the end user. Some countries, such as Denmark, require a DoC for FCMs consisting of paper and board, but this is not a general EU requirement. Industry associations like the Confederation of the European Paper Industries (CEPI) has expressed a strong interest in getting harmonized guidelines in Europe for limit values, as well as sampling and test methods for PFAS and for paper and board materials in general. They are supported by thethe International Life Science Institute (ILSI) industry association and large food companies like Nestlé.

The converters may in some cases apply the coating on-site to the paper material. In some cases, a food industry can also be the converter, e.g. for producers of microwave popcorn bags. As for the manufacturers of the paper material, they are concerned with the performance of the material, the machinability of the differently coated papers, and any extra costs associated with it. One benefit of changing away from fluorinated coatings is that gluing and printing become easier, because the fluorinated coating generally makes it difficult for any chemical to stick to the paper material, which can be of special concern in relation to set off during stacking of the material.

The importers can also accept extra costs if there is a demand for the products. The importers prefer DoCs that are based on harmonized sampling and test methods, provided by trustworthy (certified) laboratories and written in an easily understandable language. If the manufacturer of the FCMs has not provided a DoC, it is the responsibility of the Danish importer to create a DoC.

The food producers have over the past decade become one of the most influential stakeholders when it comes to market demands for safe food packaging. A clear and trustworthy DoC is also essential to food producers. This is in part related to the risk of food scandals with chemicals contaminating their foods, which will hit their brand harder in lost sales, than the paper manufacturer or converter, who is seldom stated on the packaging. Following the food scandals in 2005 where ITX from printing inks were

measured in baby milk, Nestlé estimated that they lost 600 million Euros in two days (communication with Nestlé, 2014). Nèstlé have since invested substantially in research facilities for FCMs in Europe and in China, to obtain their own trustworthy DoC and in this way control the financial risk and hence their business. They are also very active in the development of harmonized standards for DoCs and in working with authorities towards obtaining harmonized legislation and testing conditions. This work includes a phase out of the use of fluorochemicals in all their paper products, such as chocolate wrappers, paper bags for cereals, baby products, and pet foods. For the smaller food producers which do not produce their own DoC, they are concerned with the trustworthiness of the DoC, which can be difficult to evaluate for non-experts.

The retailers, such as supermarket chains, are also becoming important in the demand for safe food packaging. They typically react to consumer pressure following media coverage of chemicals of concern. The retailers are interested in obtaining safe products that the consumers will buy, and have (good) experiences with new products substituting existing packaging technology. Apart from the chemical safety, this might also include how well the packaging performs during food preparation etc. In the case of non-fluorinated microwave popcorn bags, there is a tendency for the paper to get charred or burned, possibly because the PFAS also act as flame retardants. Other concerns can be if the packaging has fat seeping through it after a long time (years) on the shelf. This was an issue for Nestlé with their food wrappers when using the surface coated instead of the internally sized paper for flexible chocolate wrappers and for pet foods, but has since been solved. In the Nordic countries, COOP Denmark has been pro-active since 2008 in searching for non-fluorinated alternatives. Since 2014 they have worked with their suppliers and managed to find non-fluorinated alternatives for their own brand for all paper and board FCMs and in other consumers goods, such as textiles. The most difficult product to find non-fluorinated alternatives for has been microwave popcorn, and as a consequence, COOP stopped the sale of microwave popcorn in their 1,200 Danish shops on 16 May 2015. COOP estimates that substitution to non-fluorinated alternatives is not more expensive than the fluorinated coatings, and is aiming to expand the phase-out of non-fluorinated alternatives to all of COOP Nordic. Finally, retailers are concerned with the trustworthiness of the DoC, which must be easy to understand for non-experts.

Compliance test laboratories are interested in having specific legislative limits, since it generates more demand for their analyses. It is also easier to communicate to their customers whether a result is above or below a set limit or a set group-limit if there are many chemicals belonging to a class of substances, as for the PFAS. Furthermore, if the group of chemicals is large it can become very expensive to analyse each compound separately, and this is disadvantageous for the customer, especially if there is a risk that the analysis did not catch some other PFAS compound, and the test is thereby not giving them the full assurance of safety. Compliance test laboratories prefer to have harmonized guidelines for testing and sampling to limit lengthy interpretations and possible disputes of their test methods and results.

A number of well-established business cases show that non-fluorinated alternatives are:

- available and functional for almost all uses of paper and board FCMs intended for various foods
- close to cost-neutral for retailers, and hence likely also for manufacturers
- less risky to use from a human health point of view, provided that the alternatives are safe
- more sustainable since they do not expose workers, the environment, and consumers to persistent chemicals during the production, use, and disposal of the coated material.

7.1.2 The task of the authorities

Currently, there is no harmonized European specific legislation for paper and board FCMs, but only the general requirements for all FCMs in Framework Regulation 1935/2004 apply. While it is required in Denmark, there is no general EU requirement for a declaration of compliance (DoC) for FCMs consisting of paper and board, as this is only a requirement for materials with harmonized European specific regulations (such as plastic). It is the assumption of the Danish Veterinary and Food Administration (DVFA) that specific regulation gives FCM business operators (i.e. producers, importers and users of FCMs) a better starting point for the risk evaluation they need to do for their products. Because without specific legislation, the FCM operators have to perform the compliance work based only on the general requirements in the framework regulation.

The authorities make periodical checks of whether the FCMs are compliant with legislation. This can be done by checking the declaration of compliance (DoC), if required by national law, or by analyses of samples. They also play an important role in guiding businesses and compliance test laboratories in the interpretation of regulations. The authorities are concerned with food safety and the risk management measures are based on risk assessment.

To ensure high food safety, the risk management measures should be controlled analytically or by document control. The control activities should preferably be cheap, reliable, harmonized and easy to communicate to non-experts. The regulation on official controls (Regulation 882/2004) sets out the general rules for the performance of official controls to verify compliance with the rules. This includes requirements for the analysis which must be followed.

Authorities are generally concerned with emerging chemicals, in this case PFAS, in FCMs on the ever-changing global market. This typically requires exploratory analyses, e.g. using specific methods to screen for and identify the emerging substances in products sampled in market surveys.

7.2 The larger perspective on risk of POPs in FCMs

Confirmatory, quantitative data is required as input to risk assessments, on which the current EU system is based. However Late Lessons from Early Warnings, provides numerous cases of chemicals for which early warning signs based on exploratory data were ignored, with both human and economic consequences that could have been avoided if earlier action had been taken. Many of those examples were halogenated persistent organic pollutants, POPs, such as organochlorine substances and the brominated flame retardants (BFRs). An unfortunate pattern repeated itself: as soon as enough confirmatory evidence was available to restrict one compound, it was substituted to other chemicals belonging to the same group but for which only limited (exploratory) data existed. Since they shared many of the same technical properties, it could be expected that they also shared some toxic properties, but without confirmatory data, a proper risk assessment could not be made and regulatory action therefore not be taken. Examples include moving from CFC to HCFC gasses and from the PBDE BFRs to the brominated phthalates and bisphenols (EEA, 2013).

Currently, there is no regulatory tool for dealing with chemicals and groups of chemicals for which exploratory research indicates a risk, but for which confirmatory research is lacking for each individual chemical, for their potential mixture effects, and for their aggregated exposures. For a majority of chemicals, too little regulation can be corrected with later measures. However, for the POPs there is no second chance to correct mistakes. If the chemicals are spread in the environment—which research and experience show that they will be (EEA, 2013) —it is extremely costly to remove the pollution, if possible at all. Examples include the short chain PFAAs which are difficult to remove from drinking water using conventional methods (Eschauzier et al. 2012b).

In the case of PFAS, being a group of poorly characterized, persistent chemicals, many of which are persistent, bioaccumulative and toxic (PBT), the question is therefore if there are other options for *Early Action Regulations* (EARs) which will limit human and environmental exposure until a proper risk assessment has been performed.

FCMs represent only one of the sources of human exposure to fluorinated chemicals. However, with every production, and every disposal of an FCM item, there is exposure for the environment and for the workers associated with it. Documentation from fluorochemical producers shows that up to 88% of the fluorochemicals added to paper are retained on the paper material, whereas 8% are bound to sludge and 4% are released into the environment with the wastewater.

By restricting the use of PFAS in paper and board FCMs, this one exposure route can be eliminated (Scheringer et al, 2014). At the same time, it will also lower the release of PFAS into the environment, and thereby also the risk of PFAS contamination of feed, food, and drinking water. Another benefit of restricting PFAS in paper FCMs is that recycled paper produced from recycled FCM paper and board also will be free from contamination with these POPs.

Integrated risk management considering exposure routes both from the FCMs (during the use phase) and from the environment (released during the production and disposal phase) is in line with the current Environmental Action Program in the EU

(European Union, 2013). It takes into account aggregate exposure from multiple sources and the need to keep recyclable resources clean in a circular resource economy (European Union, 2013).

7.3 Content of the workshop

Two group discussions were held on Day 1 and Day 2 of the workshop. The participants were divided into smaller groups, asked to reflect on some given discussion points and finally present their answers in plenum. On Day 1, three topics were covered: Toxicology, Analysis & Exposure and Risk management. On Day 2, all groups were asked to discuss the same topic: Risk management options, and the pros and cons of three given scenarios. The three scenarios are given below.

7.3.1 Outcome of the workshop

If a country decides to adopt national risk management measures on PFAS there are several options. Between the two extreme endpoints for regulation, namely a) only the framework regulation and b) full specific regulation of fluorinated substances in P&B FCMs, some intermediate risk management options exist. It has to also be considered whether single substances or groups of substances should be regulated, and whether the industry has to apply for the use of a given substance (Table 8).

Table 8: Possible elements for specific risk management measures in P&B

Elements	Chemicals	Assessment	Range	Limits
Positive list including limits of content or migration limits where necessary	Single substances or groups of substances	Based on applications or assessments from authorities	Exhaustive list (all other substances not allowed) or non-exhaustive	SML, Q_M
And / or List of substances not to be used	Single substances or Groups of substances			Limit of detection

Today, risk management of fluorinated chemicals in paper and board meant for food contact is based exclusively on the requirements in the framework regulation for FCMs (Regulation 1935/2004). The most important requirement of this regulation is that chemicals must not migrate from FCMs to food in amounts that can endanger human health. It is the responsibility of the business operator that manufactures or imports FCMs to assess the chemicals that are part of their materials and document that this requirement is fulfilled. At the present workshop, the practical options for handling this requirement for the fluorinated substances were discussed

Furthermore the following three scenarios for future risk management of fluorinated chemicals in paper and board FCMs were discussed:

- *Scenario 1*: A total ban on or restriction of the content of fluorinated chemicals, for example expressed as the total content of organically bound fluorine in the material.
- *Scenario 2*: Restrictions for groups of chemicals, e.g. PFCAs and PFSAs, and their precursors (compounds that degrade to them).
- *Scenario 3*: Restrictions for individual chemicals, e.g. a positive list of approved substances with specific migration limits, or limits for the content in the material, or a negative list of prohibited substances.

Generally, the participants of the workshop expressed most support for *Scenario 1*. Depending on how low the limit value for content in the material is set, this would also give the most cautious approach to risk management, since the use of all fluorinated substances would be managed at the same time. If the aim is a ban, it could be enforced for the content of organically bound fluorine, set close to the analytical possibilities for detection. For example, 10 µg/kg food is the limit value that applies for substances which may not be present in measurable amounts in plastic food contact materials. However, it is important that a ban can be observed by deliberately not adding these substances to the food contact material. So a limit value must take a possible background level of fluorinated chemicals present in the paper, e.g. from the water used for production of the paper, into account.

Two variants of Scenario 1 exist:

- The possibility for producers to apply for exemption from the total ban or restriction for specific substances that can enter a positive list for use in paper and board FCMs.
- The limit value can be set for migration from the paper instead of for content in the material.

The analysis of the content of total organic fluorine in the paper and board material is a more simple and affordable method compared to the analysis of individual fluorinated substances. The enforcement and compliance testing could be done by modifying and using an existing CEN method for wood chips, which is in use by a few European commercial testing laboratories. The method should be adjusted to achieve lower LODs. However, the analysis of total organic fluorine in a migrate from migration testing is not yet possible, due to lack of validated methods for analysing simulants. Furthermore, there are no harmonized methods for migration testing of paper and board, which could result in disputes over test results. However, test conditions and food simulants for plastic food contact materials could be applied, such as 50% ethanol, which is a standard simulant for emulsified foods in Regulation EU 10/2011. Food simulants for plastics are recommended for testing paper and board in the Dutch legislation and in the Council of Europe guidelines.

Scenario 2, which suggests one or several restrictions for groups of fluorinated chemicals, was least preferred by the participants of the workshop. It does have the

advantage that it relates directly to the PFAAs for which some risk assessment exists. The main drawback is that commercial tests are not yet available. Concerns were also raised regarding the difficulty of grouping the fluorinated chemicals, and that the groupings continuously need updating when new substances are used. However, since the REACH restriction for PFOA and related substances in chemicals and consumer products including FCMs has been adopted, a confirmatory CEN method for these substances can be expected in the future. The idea of summing all the PFCAs into PFOA equivalents, and all the PFSAs and PFSA precursors into PFOS equivalents, and comparing these with a TDI value of PFOA and PFOS respectively, has recently been applied in the official Danish control of PFAS in paper and board food packaging in Denmark.

Scenario 3, which suggests risk management for individual fluorinated substances in migrates or food, is most similar to the already existing harmonized specific measure for plastic FCMs. Several of the workshop participants therefore found it appealing. However, this option for risk management was also seen as the least practicable, since it requires a profound knowledge of the toxicology, function and use in the materials of the individual substances. Today, this knowledge is not accessible, but could be supplied with help from the paper producing industry etc. Confirmatory analytical methods are also unavailable for most of the polyfluorinated precursors and for the new fluorinated chemicals. If the specific fluorinated substances in paper and board were regulated in the same way as plastics, substances not allowed to be used (or where no migration is permitted) would each have a migration limit of 10 µg/kg. For comparison, the limit value for migration of PFOS, based on the current tolerable daily intake of 0.15 microgram/kg bodyweight/day (EFSA 2008) would result in a migration limit value of 9 µg/kg food. Scenario 3 only focuses on migration and human exposure during the FCM use phase, and not on the potential exposure due to environmental contamination from the production and disposal of the materials.

Conclusion

In general, since 2002, decreasing levels of PFOA and PFOS have been observed in the environment following the replacement of these substances with shorter chain PFASs. Increasing levels of short chained perfluorinated sulfonates have been observed in the environment.

There is generally insufficient human and environmental data about short chain PFAS and other fluorinated alternatives to the longer chained PFSA and PFCA. The limited data available indicates specific toxic effects on humans and the environment. However, more and deeper studies will be required to get a clearer picture of the properties of these PFAS before far-reaching conclusions can be drawn about their toxic properties.

Lack of physical-chemical data for PFAS other than PFOA and PFOS is an obstacle to environmental fate modelling. Also the lack of improved analytical methods and analytical reference substances is currently a barrier to extended studies of the many different substances in the environment and food, and to better estimating the different human exposure routes, including FCMs. In addition, sufficient toxicity data is only available for very few of the substances. Overall, the publicly available knowledge on the many different fluorinated substances on the market, including their structure, properties, use, and toxicological properties is limited.

Outlook

Data on toxicity and exposure of specific PFAS is limited, and a full risk assessment is only performed for a few substances such as PFOS and PFOA.
As PFAS are persistent organic pollutants (POPs), and in several cases bioaccumulative and toxic, a regulation that supports substitution to other persistent fluorinated alternatives must be considered carefully. The workshop supported risk management scenario 1, with the aim of reducing the total content of organically bound fluorine in paper and board FCMs.

In support of this, the level of a Danish recommended limit on total organic fluorine in paper and board FCMs was suggested by the National Food Institute, DTU Food, in 2016 (Trier et al. 2016). The limit value should take a possible background level of fluorinated chemicals present in the paper, e.g. from natural fluorine levels in wood or the water used for production of the paper, into account.

In support of such a limit level, an appropriate analytical method for determining total organic fluorine in paper and board is to be implemented and validated.

The currently recommended limit and the analytical method for its determination are under revision by the National Food Institute, DTU Food. This is due to higher

background levels in the paper and board FCMs than originally expected and uncertainties in the analytical method.

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Abbreviations

AKD	Alkyl Ketene Dimer
APCI	Atmospheric Pressure Chemical Ionization
ASA	Alkenyl Succinic Anhydride
BfR	Bundesamt für Risikobewertung (Federal Institute for Risk Assessment)
CEN	European Committee for Standardization
CoE	Council of Europe
DiPAPs	Dialkylated polyfluorinated alkyl phosphate surfactant
DTU	Technical University of Denmark
DTU-Food	DTU, the National Food Institute
EC	European Commission
ECF	Electrochemical Fluorination
EFSA	European Food Safety Authority
EIC	Extracted Ion Chromatogram
E-SEM	Environmental Scanning Electron Microscopy
EO	Ethoxylate
ESI^-	Electrospray Ionization, in the negative mode
ESI^+	Electrospray Ionization, in the positive mode
EU	European Union
FPE	Flexible Packaging Europe
FTMAP	Fluortelomer Mercapto Alkyl Phosphate (also named S-diPAPs)
FTOH	Fluorotelomer Alcohol
GC	Gas Chromatography
GMP	Good Manufacturing Practice
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
JRC	Joint Research Council (of the European Communities)
LDR	Linear Dynamic Range
LOD	Limit of Detection
MeOH	Methanol
MonoPAPs	Monoalkylated polyfluorinated alkyl phosphate surfactant
MS	Mass Spectrometer or Mass Spectrometry
MSMS	Tandem Mass Spectrometry, in space or in time
N-Et-FOSE	N-Ethyl Perfluorooctyl Sulphonamide Ethanol, $C_8F_{17}SO_2NHCH_2CH_2OH$
N-Me-FOSE	N-Methyl Perfluorooctyl Sulphonamide Ethanol, $C_8F_{17}SO_2NHCH_2OH$
NIAS	Non-Intentionally Added Substances
NMD	Negative Mass Defect
NMR	Nuclear Magnetic Resonance
OECD	Organization for Economic Co-operation and Development

PAP	A polyfluorinated Alkyl Phosphate Surfactant
PCB	Polychlorinated Biphenyl
PE	Polyethylene (HDPE: High density PE and LDPE: Low density PE)
PerPFS	Perfluorinated PFAS
PFA	Perfluorinated acid
PFAA	Perfluoro Alkyl Acids $F(CF_2)_x$-acid group
PFAS	Per- and poly-Fluorinated Alkyl Substances
PFCA	Perfluoro Carboxylic Acid
PFDA	Perfluoro Decanoic Acid, $C_9F_{19}COOH$
PFHpA	Perfluoro Heptanoic Acid, $C_6F_{12}COOH$
PFHxA	Perfluoro Hexanoic Acid, $C_5F_{11}COOH$
PFNA	Perfluoro Nonanoic Acid, $C_8F_{17}COOH$
PFOA	Perfluoro Octanoic Acid, $C_7F_{15}COOH$
PFOS	Perfluorooctane Sulphonate, $C_8F_{17}SO_3H$
PFOSA	Perfluorooctane Sulphonamide, $C_8F_{17}SO_2NH_2$
PFPA	Perfluoro Pentanoic Acid, C_4F_9COOH
PFPE	Perfluoro Polyether
PFAS	Poly- or Perfluorinated Alkyl Surfactant
PFSA	Perfluoro Sulphonic Acid
PIM	Plastics Implementing Measures
PolyPFAS	Polyfluorinated PFAS
POP	Persistent Organic Pollutant
PP	Polypropylene
PTFE	Polytetrafluoroethylene (such as Teflon)
QM	Quantity in the Material
QMA	Quantity per Area of the Material
QqQ	Tandem Quadrupole (MSMS)
QLIT	Quadrupole Linear Ion Trap
QTOF	Quadrupole Time-Of-Flight (MS or MSMS)
R	Resolution
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
S-diPAPs	Sulphonate Dialkyl Polyfluorinate Alkyl Phosphate Surfactant (=FTMAP)
SIM	Single Ion Monitoring
SML	Specific Migration Limit
S/N	Signal-to-Noise ratio
SRM	Single Reaction Monitoring
SPE	Solid Phase Extraction
TC	Technical Committee
TDI	Tolerable Daily Intake
Teflon	A commercial name for PTFE
TIC	Total Ion Chromatogram
T-PFOS	Technical PFOS
TriPAPS	Trialkyl Polyfluorinated Alkyl Phosphate Surfactant
US-EPA	United States Environmental Protection Agency

US-FDA	United States food and Drug Administration
UHPLC	Ultrahigh Pressure Liquid Chromatography
UNEP	United Nations Environmental Programme

Appendices

Appendix 1

Overview of fluorinated compounds allowed in paper and board (for temperatures up to 90 °C) in contact with food by the German Bundesamt für Risikobewertung (BfR) 2016.

Table 1: Fluorinated substances in BfR recommendation no 36, for paper and board at temperatures up to 90 °C (July 2016)

Substance	Q_M	Remarks
Phosphoric acid esters of ethoxylated perfluoropolyetherdiol	1,5% (dry weight)	
Perfluoropolyetherdicarbonic acid, ammonium salt	0,5% (dry weight)	Not for aqueous or alcoholic foods
Copolymer with 2,2'-ethylendioxydiethyldimethacrylat, 2-hydroxyethyl-methacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, acetate and/or malate	1,2% (dry weight)	
2-propen-1-ol, reaction products with 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane, de-hydroiodated reaction products with epichlorohydrine and triethylene tetramin with a fluorine content of 54%	0,5% (dry weight)	
Copolymer of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylacrylate, 2-hydroxyethylacrylate, polyethylenglycolmonacrylate and polyethylenglycoldiacrylate with a fluorine content of 35,4%	0,4% (dry weight)	
Copolymer with methacrylic acid, 2-hydroxyethylmethacrylate, polyethylenglycolmonacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylacrylate, sodium salt with a fluorine content of 45,1%	0,8% (dry weight)	
Copolymer med methacrylic acid, 2-diethylaminoethylmethacrylate, acrylic acid and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, acetate with a fluorine content of 45,1%	0,6% (dry weight)	
Copolymer of methacrylic acid, 2-dimethylaminoethylmethacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, acetate with a fluorine content of 44,8%	0,6% (dry weight)	
Poly (hexafluoropropyleneoxide), polymer with 3-N-methylaminopropylamine, N, N-dimethyldipropylenetriamine and poly (hexamethylenediisocyanate) with a fluorine content of 59,1%	4 mg/dm²	
Reaction product of hexamethylene-1,6-diisocyanate (homopolymer), transformed with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol with a fluorine content of 48%	0,16% (dry weight)	
Copolymer of 2-dimethylaminoethylmethacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, N-oxide, acetate, with a fluorine content of 45%	4 mg/dm²	
Copolymer with 2-hydroxyethylmethacrylate, methacrylic acid, itaconic acid and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, sodium salt	24 mg/dm²	
Copolymer with 2-hydroxyethylmethacrylate, vinylpyrrolidon, acrylic acid and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylacrylate, sodium salt, with a fluorine content of 41,9%	1%	

Table 2: Substances, recommended by BfR for coating of paper and board for baking purpose (recommendation no 36/2, July 2016)

Substance	Q_M
Phosphoric acid ester of ethoxylated perfluoropolyetherdiol	1,5% (dry weight)
Copolymer with 2-diethylaminoethylmethacrylate, 2,2'-ethylendioxydiethyldimethacrylate, 2-hydroxyethylmethacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate, acetate and/or malate	1,2% (dry weight)
Copolymer with methacrylic acid, 2-hydroxyethylmethacrylate, polyethylenglycolmonacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylacrylate, sodium salt with a fluorine content of 45,1%	0,8% (dry weight)

Note: QM: Maximum level in the material.

Appendix 2

Overview of fluorinated substances listed in the Council of Europe "Policy statement concerning paper and board materials and articles intended to come into contact with foodstuffs", Version 4 – 12.02.2009.

Table 3: List 1 of additives (list of additives assessed)

PM/ REF No	CAS No	Name	SCF-L	Restrictions and/or Specifications	ADI/TDI mg/kg bw
43680	000075-45-6	Chlorodifluoromethane	2	SML = 6 mg/kg	0,1
48460	000075-37-6	1,1-Difluoroethane	3		
-	030381-98-7	Bis[2-[N-ethyl(perfluorooctane)sulphonamido]ethyl] phosphate, ammonium salt[1]	-	To be fixed	
-	-	2-(Diethylamino)ethyl methacrylate – 2,3-epoxypropyl methacrylate – perfluoroalkyl(C4-C18)ethyl acrylate[2]	-	To be fixed	
-	-	2-(Dimethylamino)ethyl methacrylate – perfluoroalkylethyl acrylate – vinyl acetate, copolymer[2]	-	To be fixed	
-	067969-69-1	N-Ethyl-N-(2-hydroxyethyl)-perfluorooctanesulphonamide phosphate, diammonium salt[1]	-	To be fixed	
-	479029-28-2	Methacrylic acid, 2-(dimethylamino)ethyl ester, polymers with gamma-omega-per- fluoro-C8-14-alkyl acrylate, acetates, N-oxides[2]	-	To be fixed	

Note: [1]PFSA precursors.
[2]PFCA precursors.

Table 4: Temporary appendix to list 1 of additives (list of additives approved by partial agreement member states or by fda, applying evaluation criteria at the time of their approval)

PM/ REF No	CAS No	NAME	SCF-L	Restrictions and/or Specifications
-	-	Phosphoric acid, mono- and bis(gamma, omega-perfluoroalkyl) esters, compounds with diethanolamine[1]	-	To be fixed

Note: [1] PFCA precursors

Table 5: List 2 of additives (list of additives not yet assessed)

PM/ REF No	CAS No	NAME	SCF-L	Restrictions and/or Specifications
47360	000075-71-8	Dichlorodifluoromethane	7	To be fixed
-	092265-81-1	2,3-Epoxypropyl methacrylate - 2-ethoxyethyl acrylate - N-methyl-perfluorooctanesulphonamido-ethyl acrylate – trimethyl ethanol ammonium chloride methacrylate, copolymer[1]	-	To be fixed
-	000354-33-6	Pentafluoroethane	-	To be fixed
-	068310-75-8	(Perfluorooctylsulphonylamino propyl)-trimethyl ammonium iodide[1]	-	To be fixed
-	000811-97-2	1,1,1,2-Tetrafluoroethane	-	To be fixed
93920	000075-69-4	Trichlorofluoromethane	7	To be fixed
-	000420-46-2	1,1,1-Trifluoroethane	-	To be fixed
94480	026523-64-8	Trifluorotrichloroethane	7	To be fixed
25120	000116-14-3	Tetrafluoroethylene	3	SML = 0.05 mg/kg

Note: [1]PFSA precusors.

Table 6: Monomers approved by Partial Agreement member states or by FDA, applying evaluation criteria at the time of their approval

PM/ REF No	CAS No	NAME	SCF-L	Restric-tions and/ or Specifi-cations	ADI/TDI mg/kg bw
-	025268-77-3	Acrylic acid, N-methyl-perfluorooctanesulphonamido-ethyl ester[1]	-	To be fixed	

Note: [1]PFSA precusors.

PM/REF No : The EU packaging material reference number of the substance.
CAS No: The Chemical Abstracts Service Registry Number of the substance.
NAME: The chemical name of the substance or the substance group.
SCF-L: The number of the list in which the substance is classified by the Scientific Committee for food / EFSA.
Restrictions and/or: Restrictions and/or specifications related to the substance specifications.

Appendix 3

Table 7: **Authorized fluorinated substances in Commission regulation on plastic materials and articles intended to come into contact with food, Regulation (EU) no 10/2011 (30.12.2011) including the amendment of Commission Implementing Regulation (EU) No 321/2011 of 1 April 2011 and Commission Regulation (EU) No 1282/2011 of 28 November 2011 (compiled August 24th 2012).**

FCM No.	Ref. No.	CAS No.	Substance name	Additive or polymer production aid	Monomer	SML mg/kg*	Restrictions and specifications
131	*48460*	*0000075-37-6*	*1,1-difluoroethane*	*yes*	*no*		
132	26140	0000075-38-7	vinylidene fluoride	no	yes	5	
134	*43680*	*0000075-45-6*	*chlorodifluoromethane*	*yes*	*no*	*6*	*Content of chlorofluoromethane less than 1 mg/kg of the substance*
148	14650	0000079-38-9	chlorotrifluoroethylene	no	yes	ND	
281	25120	0000116-14-3	tetrafluoroethylene	no	yes	0,05	
282	18430	0000116-15-4	hexafluoropropylene	no	yes	ND	
337	*15820*	*0000345-92-6*	*4,4'-difluorobenzophenone*	*no*	*yes*	*0,05*	
391	22932	0001187-93-5	perfluoromethyl perfluorovinyl ether	no	yes	0,05	Only to be used in anti-stick coatings
423	22937	0001623-05-8	perfluoropropylperfluorovinyl ether	no	yes	0,05	
468	71960	0003825-26-1	perfluorooctanoic acid, ammonium salt[2]	yes	no		Only to be used in repeated use articles, sintered at high temperatures
854	71943	0329238-24-6	perfluoro acetic acid, α-substituted with the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropyl oxy groups	yes	no		Only to be used in concentrations up to 0,5% w/w in the polymerization of fluoro-polymers that are processed at temperatures at or above 340 °C and are intended for use in repeated use articles
860	71980	0051798-33-5	perfluoro[2-(poly(n-propoxy))propanoic acid]	yes	no		Only to be used in the polymerization of fluoropolymers that are processed at temperatures at or above 265 °C and are intended for use in repeated use articles

Continued

FCM No.	Ref. No.	CAS No.	Substance name	Additive or polymer production aid	Mono-mer	SML mg/kg*	Restrictions and specifications
861	71990	0013252-13-6	perfluoro[2-(n-propoxy)propanoic acid]	yes	no		Only to be used in the polymerization of fluoropolymers that are processed at temperatures at or above 265 °C and are intended for use in repeated use articles.
896	71958	0958445-44-8	3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt	yes	no		Only to be used in the polymerization of fluoropolymers when processed at temperatures higher than: - 280 °C for at least 10 minutes, - 190 °C up to 30% w/w for use in blends with polyoxymethylene polymers and intended for repeated use articles.
926	71955	0908020-52-0	perfluoro[(2-ethyloxy-ethoxy)acetic acid], ammonium salt	yes	no		Only to be used in the polymerization of fluoropolymers that are processed at temperatures higher than 300 °C for at least 10 minutes.
973	22931	0019430-93-4	(perfluorobutyl)ethylene	no	yes		Only to be used as a co-monomer up to 0,1% w/w in the poly-merization of fluoropolymers, sintered at high temperatures.

Note: * SML: Specific migration limit for the substance in mg per kg food.
FCM: Food contact materil.
ND: Non detectable.
Italic: The compound contains less than 3 fluor atoms, and does not qualify as a polyfluorinated compound. They have been included for the chlorodifluoromethane monomer, which is used to make a polyfluorinated polymer, and for 1,1-difluoroethane which is a CFC gas.

Appendix 4

US FDA (Updated 2015)

http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/cfrsearch.cfm?fr=176.170

. January 22nd by P. Honigfort, US FDA; Xenia Trier Jan 27th 2015

PFCA precursors are marked in light grey. PFSA precursors are in white background

Table 8: Overview of fluorinated substances listed in the US FDA list of chemicals intended for paper and board for food contact". Greaseproofing agents listed in 21 CFR 176.170.

Substance as listed in 21 CFR 176.170	Perfluorocarboxylic acid or perfluoroalkyl sulfonate based
Ammonium bis(N-ethyl-2-perfluoroalkylsulfonamido ethyl) phosphates, containing not more than 15% ammonium mono (N-ethyl-2-perfluoroalkylsulfonamido ethyl) phosphates, where the alkyl group is more than 95% C8 and the salts have a fluorine content of 50.2% to 52.8% as determined on a solids basis[1]	perfluoroalkyl sulfonate
Diethanolamine salts of mono- and bis (1H,1H,2H,2H perfluoroalkyl) phosphates where the alkyl group is even-numbered in the range C8-C18 and the salts have a fluorine content of 52.4% to 54.4% as determined on a solids basis[2]	perfluorocarboxylic acid
Pentanoic acid, 4,4-bis [(gamma-omega-perfluoro-C8-20-alkyl)thio] derivatives, compounds with diethanolamine (CAS Reg. No. 71608-61-2)2	perfluorocarboxylic acid
Perfluoroalkyl acrylate copolymer (CAS Reg. No. 92265-81-1) containing 35 to 40 weight percent fluorine, produced by the copolymerization of ethanaminium,N,N,Ntrimethyl-2-[(2-methyl-1-oxo-2-propenyl)-oxy]-, chloride; 2-propenoic acid, 2-methyl-, oxiranylmethyl ester; 2-propenoic acid, 2-ethoxyethyl ester; and 2-propenoic acid, 2-(heptadecafluoro-octyl)sulfonyl] methyl amino]ethyl ester*[1]	perfluoroalkyl sulfonate
Perfluoroalkyl substituted phosphate ester acids, ammonium salts formed by the reaction of 2,2-bis[([gamma], [omega]-perfluoro C_4-20 alkylthio) methyl]-1,3-propanediol, polyphosphoric acid and ammonium hydroxide[2]	perfluorocarboxylic acid

Note: [1]PFSA precursors.
[2]PFCA precursors.

Table 9: Overview of fluorinated substances listed in the US FDA list of chemicals intended for food contact. http://www.mindfully.org/Food/2005/Food-Contact-Substances-FDA15feb05.htm. Taken from Trier 2011 (thesis); updated June 2012 by Trier, DTU Food. Updated January 22nd 2015 by P. Honigfort, US FDA.

No.	CAS No	Name	Used in	Note	Restriction	Max %
17	-	A perfluorocarbon-cured elastomer (PCE) produced by terpolymerizing tetrafluoroethylene (CAS Registry No. 116-14-3), perfluoro (2,5-dimethyl- 3,6-dioxanone vinyl ether) (CAS Registry No. 2599-84-0) and perfluoro (6,6-dihydro- 6-iodo- 3-oxa- 1-hexene) (CAS Registry No. 106108-22-9) and subsequent curing of the terpolymer (CAS Registry No. 106108-23-0) by crosslinking with triallylcyanurate (CAS Registry No. 101-37-1) and vulcanizing with 2,5-dimethyl- 2,5-di (t-butylperoxy) hexane (CAS Registry No. 78-63-7), as a 68% dispersion on finely divided silica[3]	In the fabrication of vulcanized molded parts for food processing equipment, such as o-rings, gaskets, diaphrams and other materials, that function primarily in sealing applications [3]	Greene, Tweed and Company, Inc. Entry date: Mar 30, 2000[3]	EA/ FONSI [3]	
59*	220459-70-1[2]	Glycine, N,N-bis[2-hydroxy-3-(2-propenyloxy)propyl]-, monosodium salt, reaction products with ammonium hydroxide and pentafluoroiodoethane-tetrafluoroethylene telomer	The FCS will be used as an oil and grease-resistant treatment for paper and paperboard intended for food-contact use.[2]	Ciba Specialty Chemicals Corporation (now BASF corp.) Entry date: August 16, 2000[2]	EA/ FONSI[2]	
101	-	Perfluorocarbon cured elastomers produced by polymerizing perfluoro(methyl vinyl ether) (CAS Reg. No. 1187-93-5) with tetrafluoroethylene (CAS Reg. No. 116-14-3) and perfluoro(8-cyano -5-methyl -3,6-dioxa -1-octene) (CAS Reg. No. 69804-19-9), followed by curing with trimethylallyl isocyanurate (CAS Reg. No. 6291-95-8) and/or triallyl isocyanurate (CAS Reg. No. 1025-15-6), and with 2,5 -dimethyl -2,5-di (t-butylperoxy) hexane (CAS Reg. No. 78-63-7) and as further described in this notification. [3]	For use in the fabrication of articles intended for repeated use in contact with food. [3]	DuPont Dow Elastomers L.L.C. Entry date: December 19, 2000[3]	EA/ FONSI [3]	
126		1,9-Decadiene,3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-, polymer with tetrafluoroethene and trifluoro(trifluoromethoxy)ethene (CAS Reg. No. 190062-24-9), manufactured and characterized as further described in the notification.[4]	As a gasket or seal for food processing equipment. [4]	Solvay Solexis S.p.A. Entry date: July 21, 2001[4]	CAT. EXCL. 21 CFR 25.32 (j) [4]	
127		1-Propene,1,1,2,3,3,3-hexafluoro-, polymer with 1,1-difluoroethene and tetrafluoroethene (CAS Reg. No. 25190-89-0) modified with triallyl isocyanurate and 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-diene, manufactured and characterized as further described in the notification. [4]	As a gasket or seal for food processing equipment. [4]	Solvay Solexis S.p.A. Entry date: July 21, 2001[4]	CAT. EXCL. 21 CFR 25.32 (j) [4]	
128		A copolymer of tetrafluoroethylene (TFE) and perfluoromethylvinyl ether (PFMVE) (CAS Reg. No. 26425-79-6) modified with 1,3,5-triallyl isocyanurate (TAIC) and 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-diene, manufactured and characterized as further described in the notification. [4]	As a gasket or seal for food processing equipment. [4]	Solvay Solexis S.p.A. Entry date: July 21, 2001[4]	CAT. EXCL. 21 CFR 25.32 (j) [4]	

continued

No.	CAS No	Name	Used in	Note	Restriction	Max %
129		Ethene, tetrafluoro-, polymer with 1,1-difluoroethene and trifluoro(trifluoromethoxy)ethene (CAS Reg. No. 56357-87-0) modified with 1,3,5-triallyl isocyanurate (TAIC) and 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-diene, manufactured and characterized as further described in the notification. [4]	As a gasket or seal for food processing equipment. [4]	Solvay Solexis S.p.A. Entry date: July 21, 2001[4]	CAT. EXCL. 21 CFR 25.32 (j) [4]	
187		Fluorinated polyurethane anionic resin (CAS Reg. No. 328389-91-9) prepared by reacting perfluoropolyether diol (CAS Reg. No. 88645-29-8), isophorone diisocyanate (CAS Reg. No. 4098-71-9), 2,2-dimethylolpropionic acid (CAS Reg. No. 4767-03-7), and triethylamine (CAS Reg. No. 121-44-8). [3]	As a water and oil repellent in the manufacture of paper and paperboard. [3]	Solvay Solexis S.p.A. Entry date: March 23, 2002[3]	CAT. EXCL. 21 CFR 25.32 (i) [3]	
195		Diphosphoric acid, polymers with ethoxylated reduced Me esters of reduced polymerized oxidized tetrafluoroethylene (CAS Reg. No. 200013-65-6). This substance is also known as: phosphate esters of ethoxylated perfluoroether, prepared by reaction of ethoxylated perfluoroether diol (CAS Reg. No. 162492-15-1) with phosphorous pentoxide (CAS Reg. No. 1314-56-3) or pyrophosphoric acid (CAS Reg. No. 2466-09-3). [3]	As a water and oil repellent in the manufacture of paper and paperboard. [3]	Solvay Solexis S.p.A. Entry date: May 14, 2002[3]	CAT. EXCL. 21 CFR 25.32 (i) [3]	
206 *	247047-61-6	Copolymer of 2-perfluoroalkylethyl acrylate, 2-N,N-diethylaminoethyl methacrylate, and glycidyl methacrylate. [2]	The FCS will be used as an oil and grease-resistant treatment for paper and paperboard intended for food-contact use. [2]	DuPont Chemical Solutions Enterprise[2] Entry date: June 12, 2002[2]	EA/ FONSI	
245		A perfluorocarbon cured elastomer (PCE) produced by terpolymerizing tetra-fluoroethylene, (CAS Reg. No. 116-14-3), perfluoromethyl vinyl ether (CAS Reg. No. 1187-93-5), and perfluoro-6,6-dihydro-6-iodo-3-oxa-1-hexane (CAS Reg. No. 106108-22-9), and subsequent curing of the terpolymer (CAS Reg. No. 193018-53-0) with triallylisocyanurate (CAS Reg. No. 1025-15-6) and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (CAS Reg. No. 78-63-7). [3]	In the fabrication of molded parts for food processing equipment, such as o-rings, gaskets, diaphragms and other materials, that function primarily in sealing applications. [3]	Greene, Tweed and Company, Inc. Entry date: August 13, 2002[3]	CAT. EXCL. 21 CFR 25.32 (j) [3]	
246		Fluorocarbon cured elastomer produced by copolymerizing tetrafluoroethylene (CAS Reg. No. 116-14-3) and propylene (CAS Reg. No. 115-07-01) and subsequent curing of the copolymer (CAS Reg. No. 27029-05-6) with triallylisocyanurate (CAS Reg. No. 1025-15-6) and 2,2'bis-(t-butylperoxy)diisopropylbenzene (CAS Reg. No. 25155-25-3).	In the fabrication of molded parts for food processing equipment, such as o-rings, gaskets, diaphragms and other materials, that function primarily in sealing applications.	Greene, Tweed and Company, Inc. Entry date: August 13, 2002	CAT. EXCL. 21 CFR 25.32 (j)	

continued

No.	CAS No	Name	Used in	Note	Restriction	Max %
247		A perfluorocarbon cured elastomer (PCE) produced by terpolymerizing tetrafluoroethylene, (CAS Reg. No. 116-14-3), perfluoro-2,5-dimethyl-3,6-dioxanonane vinyl ether (CAS Reg. No. 2599-84-0), and perfluoro-6,6-dihydro-6-iodo-3-oxa-1-hexene (CAS Reg. No. 106108-22-9), and subsequent curing of the terpolymer (CAS Reg. No. 106108-23-0) with triallylisocyanurate (CAS Reg. No. 1025-15-6) and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (CAS Reg. No. 78-63-7). [3]	In the fabrication of molded parts for food processing equipment, such as o-rings, gaskets, diaphragms and other materials, that function primarily in sealing applications. [3]	Greene, Tweed and Company, Inc. Entry date: August 13, 2002[3]	CAT. EXCL. 21 CFR 25.32 (j) [3]	
255*		3-cyclohexane-1-carboxylic acid, 6-((di-2-propenylamino)carbonyl)-,(1R,6R), reaction products with pentafluoroiodoethane-tetrafluoroethylene telomer, ammonium salts.	The FCS will be used as an oil repellent sizing agent in the production of paper and paperboard.	Ciba Specialty Chemicals Corporation Entry date: September 5, 2002	CAT. EXCL. 21 CFR 25.32 (i)	
260		Tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride copolymers (CAS Reg. No. 25190-89-0).	As a processing additive for polyolefins for use in contact with food.	Dyneon LLC Entry date: October 3, 2002	CAT. EXCL. 21 CFR 25.32 (i)	
278		Copolymer of tetrafluoroethylene, perfluoromethylvinylether and 1-iodo-2-bromo-tetrafluoroethane intended to be cross-linked with triallylisocyanurate. [3]	As an o-ring or gasket in food-processing machinery. [3]	Unimatec Co., Ltd. Entry date: November 27, 2002[3]	CAT. EXCL. 21 CFR 25.32 (j) [3]	
311*		Copolymers of 2-perfluoroalkylethyl acrylate, 2-N,N-diethylaminoethyl methacrylate, and glycidyl methacrylate. [2]	For use as an oil or grease resistant treatment for paper and paperboard intended for single service use in microwave heat-susceptor packaging; the food-contact substance is intended to contact all food types. [2]	DuPont Chemical Solutions Enterprise Entry date: April 15, 2003[2]	EA /FONSI[2]	
314		2-Propen-1-ol, reaction products with pentafluoroiodoethane-tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylenetetramine (CAS Reg. No. 464178-90-3).	As an oil/grease resistant sizing agent employed prior to the sheet-forming operation in the manufacture of paper and paperboard for single use applications.	Hercules, Inc. Entry date: April 15, 2003	CAT. EXCL. 21 CFR 25.32 (i)	
338 *	247047-61-6	Copolymers of 2-perfluoroalkylethyl acrylate, 2-N,N-diethylaminoethyl methacrylate, and glycidyl methacrylate. [2]	For use as an oil or grease resistant treatment for paper and paperboard intended for food-contact use.	DuPont Chemical Solutions Enterprise Entry date: August 19, 2003[2]	EA /FONSI[2]	

continued

No.	CAS No	Name	Used in	Note	Restriction	Max %
398		Perfluoropolyether dicarboxylic acid (CAS Reg. No. 69991-62-4), ammonium salt.[3]	As an oil and water repellent in the manufacture of food-contact paper and paperboard.[3]	Solvay Solexis S.p.A. Entry date: April 13, 2004[3]	CAT. EXCL. 21 CFR 25.32 (i)[3]	
402		A copolymer of tetrafluoroethylene and perfluoromethylvinyl ether (CAS Reg. No. 26425-79-6) \ modified with 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-diene and 1,3,5-triallyl cyanurate or 1,3,5-triallyl isocyanurate.[3]	As a gasket or seal for food processing equipment.[3]	Precision Polymer Engineering, Ltd. Entry date: July 2, 2004[3]	CAT. EXCL. 21 CFR 25.32 (j)[3]	
416		Diphosphoric acid, polymers with ethoxylated reduced methyl esters of reduced polymerized oxidized tetrafluoroethylene (CAS Reg. No. 200013-65-6). Fomblin HC/P2-1000. This substance is also known as phosphate esters of ethoxylated perfluoroether, prepared by reaction of ethoxylated perfluoroether diol (CAS Reg. No. 162492-15-1) with phosphorous pentoxide (CAS Reg. No. 1314-56-3) or pyrophosphoric acid (CAS Reg. No. 2466-09-3).[3]	As a water and oil repellent in the manufacture of paper and paperboard.[3]	Solvay Solexis S.p.A. Entry date: July 27, 2004[3]	CAT. EXCL. 21 CFR 25.32 (i)[3]	
FCN 628*	479029-28-2	Copolymer of 2-perfluoroalkylethyl acrylate, 2-(dimethylamino)ethyl methacrylate, and oxidized 2-(dimethylamino)ethyl methacrylate (CAS REG No. 479029-28-2)[2]	Greaseproofing agent for paper and board	Clariant Entry date: October 10, 2006[2]	CAT. EXCL. 21 CFR 25.32 (i)[3]	
FCN 646*	870465-08-0	Copolymers of 2-perfluoroalkylethyl acrylate, 2-N,N-diethylaminoethyl methacrylate, glycidyl methacrylate, acrylic acid, and methacrylic acid[2]	Greaseproofing agent for paper and board[2]	DuPont Chemical Solutions Enterprise Entry date: September 30, 2006[2]	CAT. EXCL. 21 CFR 25.32 (i) and EA/FONSI[3]	
?*	392286-82-7	3-cyclohexene-1-carboxylic acid, 6-[(di-2-propenylamino) carbonyl]-, sodium salt, reaction products with pentafluoroiodoethane-tetrafluoroethylene telomer, ammonium salts	Greaseproofing agent for paper and board	BASF		

Note: *Withdrawn by the company from the US FDA FCN list, due to health concerns, (2012-07-06), ttp://www.foodmate.com/news/201207/news_2788.html

1 PFSA precursors.

2 PFCA precursors.

3 PFPEs.

4 Other long fluorocarbon chains.

Appendix 5

The Netherlands

The Netherlands has national rules for food contact materials of paper and board. Table 10 shows the substances permitted in paper and board food packaging materials that can be used for temperatures up to 80 °C. In addition, the Netherlands has a total limit for migration of the permitted fluorinated substances of 1 mg fluorine / kg of food.

Table 10: Fluorinated compounds allowed in paper and board in contact with food (up to 80 °C) in the Netherland (januar 2017)

Substance	Cas. no.	Limit
Diphosphoric acid, polymers with ethoxylated, reduced methyl esters of reduced polymerized and oxidized tetrafluoroethylene	200013-65-6	SML: 0,05 mg/kg
Ammoniumbis (N-ethyl-2-perfluorooctansulfonamidethyl) phosphate with maximum content of 15% ammoniummono (N-ethyl-2-perfluorctansulfonamidethyl) phosphate	-	SML: 3 mg/kg
Copolymers of 2- (perfluoroctylsulfonylaminomethyl) ethylmethacrylate, 2,3-epoxypropylmethacrylate, ethoxyethylacrylate and methacryloylmethyl-trimethylammoniumchloride	-	-
Perfluoralkyl (C_6-C_{16}) (C_6-C_{18}) phosphates of bis (2-hydroxyethyl) amine	-	Q_M 1%, SML: 1 mg/kg

Note: SML: specific migration limit, QM: Maximum level in the material.

The Netherlands does not allow the use of fluorinated substances in paper and board food contact materials intended for baking and hot filtration.

Appendix 6

Italy

Italy has national rules for paper and board food contact materials. Tabel 11 list the substances that are permitted in paper and board food contact materials.

Table 11: Fluorinated compounds allowed in Italy in paper and board in contact with food

Substance	Q_M
Copolimer perfluoroalkylacrylate	0,5%
Diphosphoric acid, polymers with methyl esters reduced ethoxylates oxidized reduced polymerized tetrafluoro ethylene	1,5%
Ammonium-bis- (N-ethyl-2-perfluorooktansulfonamidethyl) phosphate with maximum content of 15% ammonium mono (N-ethyl-2-perfluoroktansulfonamidethyl) phosphate	0,5%
Ammonium salts of esters from reaction with 2,2'-bis perfluoralkyl substituted phosphoric acid formates [(alfa, omega-perfluoro C_4-C20 alkylthio) methyl] -1,3-propanediol, polyphosphoric acid and ammoniumhydroxide	0,44%
Acetic salts of the copolymer of perfluoroalkylethylacrylate, vinyl acetate and dimethyl aminoethylmetacrylate	1,25% (pasta), 0,5% (other products)

Note: QM: Maximum level in the material.

Appendix 7

Belgium

Belgium has national rules for food contact materials of paper and board. Table 12 shows the substances permitted in paper and board food contact materials for aqueous and fatty foods.

Table 12: Fluorinated compounds allowed in paper and board for contact with aqueous and fatty foods

Substance	Q_M
Ammonium-bis- (N-ethyl-2-perfluoralkylsulfonamidoethyl) phosphate cannot contain more than 15 % ammoniummono(N-ethyl-2-perfluoralkylsulfonamidoethyl) phosphate	8,3 mg/dm², 4,4 mg F/dm²
Diethanolaminosalts of mono- and bis (1H, 1H, 2H, 2H-perfluoroalkyl) phosphates	-

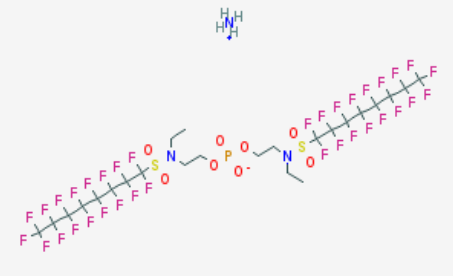
Appendix 8

Overview of fluorinated substances listed in the National Standard of the People's Republic of China list of chemicals intended for food contact', Hygeinic standard of the People's Republic of China, GB9685-2016, Implementation date October 2016.

Table 13: Extracted manually from GB 9685-2016 Plus (English translation) - search word: fluor

		CAS No.	Material
FCA0028	1-Propene, 1,1,2,2,3,3,3-hexafluoro	116-15-4	PE, PP, PA
FCA0029	1-Propene, 1,1,2,2,3,3,3-hexafluoro - polymer with 1,1-difluoroethene	9011-17-0	PE, PP and rubber
FCA0030	1-Propene, 1,1,2,2,3,3,3-hexafluoro - polymer with 1,1-difluoroethene and tetrafluoroethene	24937-79-9	PE, PP and rubber
FCA0031	1-Propene, 1,1,2,2,3,3,3-hexafluoro - polymer with tetrafluoroethene	25190-89-0	Plastics
FCA0032	Ethene, 1,1-dichlroro		Plastics
FCA0153	12H-Dibenzo(d,g)(1.3.2)dioxaphosphocin, 2,4,8,10-tetrakis(1,1-dimethylethyl)-6-fluoro-12-methyl-		Additive for adhesive
FCA0315	1-Hexene, 3,3,4,4,5,5,6,6,6,-nonafluoro-, polymer with ethane and tetrafluorethene	68258-85-5	in manufacture (polymer)
FCA0446	Benzamide, 3,3'-((2-chloro-5-methyl-1, 4-phenylene)bis(imino(1-acetyl-2-oxo-2,1-ethanediyl)azo)) bis(4-chloro-N-(2-(4-chlorophenoxy)-5-trifluoromethyl)phenyl)-		PE, PP, PS, AS, ABS, PA, PET, PC, PVC, PVDC, UP
FCA0446	Benzamide, 3,3'-((2-chloro-5-methyl-1, 4-phenylene)bis(imino(1-acetyl-2-oxo-2,1-ethanediyl) azo))bis(4-chloro-N-(2-(4-chlorophenoxy)-5-trifluoromethyl)phenyl)-(C.I. Pigment Yellow 128)	79953-85-8	Manufacture (colourant), inks
FCA0452	Butamamide, N-(2,2-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo-2-((2-(trifluoromethyl)phenyl)azo)-	68134-22-5	Manufacture (colourant), inks
FCA0623	2-propenoic acid, 2-hydroxyethyl ester, polymer with α-(1-oxo-2-propen-1-yl)-w-hydroxypoly(oxy-1, 2-ethanediyl), α-(1-oxo-2-propen-1-yl)-w-((1-oxo-2-propen-1-yl)oxo)poly(oxy-1,2-ethanediyl) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluor	1012783-70-8	A glycol-acid, for paper and board
FCA0731	Methane, chlorodifluoro	75-45-6	PE, PP, PS, AS, ABS, PA, PET, PC, PVC, PVDC, UP
FCA0746	Diphosphoric acid, polymers with ethoxylated Me esters of reduced polymd. oxidized tetrafluoroehtylene	200013-65-6	Paper and board
FCA0930	Ethene, 1,1-difluoro-, homopolyer		in manufacture (polymer)
FCA0931	1-Propene, 1,1,2,2,3,3,3-hexafluoro - polymer with tetrafluoroethene	25067-11-2	Additive for rubber
FCA0933	Ethene, tetrafluoro-, homopolymer	9002-84-0	PE, PP, PS, PET, PC, ABS, PVC, PVDC
FCA1020	Ethene, chlorotrifluoro-, polymer with 1,1-difluroethene	9010-75-7	Additive for rubber
FCA1093	Ethene, trifluoro(trifluoromethoxy)-	1187-93-5	Additive for rubber

		CAS No.	Material
FCA1143	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)	30381-98-7	Paper and board, sizing agent



Note: This standard shall supersede GB 9685-2008 (Hygienic Standard for Use of Additives in Food Containers and Packaging Materials). In this standard, main changes compared with GB 9685-2008 are shown as follows: - 3 perfluorochemicals including perfluoroalkyl acrylate copolymer used in the manufacturing of paper and paper board for food contact are removed.

Source: by Xenia Trier, 21. July 2017.

Overview of fluorinated substances listed in the National Standard of the People's Republic of China list of chemicals intended for food contact', Hygeinic standard of the People's Republic of China, GB9685-2008, Implementation date July 2008.

Table 14: GB11678-89 Hygienic standard for polytetrafluorethylene used as inner coating of food container

CAS No	Name	Used in	Note	Restriction	Max %
9002-84-0	Polytetrafluoroethylene	-	Distilled water, 100 °C for 0.5h, then put it at ambient condition (24h)	F content < 0.2 mg/L	

Table 15: GB 9685-2008 Hygienic standards for uses of additives in food containers and packaging materials

CAS No	Name	Used in	Note	Restriction SML mg/kg	Max %
116-15-4	1,1,2,3,3,3-Hexafluoro-1-propene	Plastics (PE,PP,PA)		ND	0.2%
9011-17-0	Polymer of 1,1,2,3,3,3-Hexafluoro-1-propene and 1,1-difluoroethylene 1,1-difluoroethylene	Plastics (PE,PP) and rubber Adhesive, rubber	MW of polymer > 70 000 Dose as necessary	ND 5.0 30.0	0.1%
25190-89-0	Co-Polymer of 1,1,2,3,3,3-Hexafluoro-1-propene and 1,1-difluoroethylene and Tetrafluoroethene 1,1-difluoroethylene Tetrafluoroethene	Plastics (PE,PP) Rubber	MW of polymer > 100 000 Dose as necessary	ND 5.0 0.05 5.0 0.05	0.2%

continued

CAS No	Name	Used in	Note	Restriction SML mg/kg	Max %
75-45-6	Chlorodifluoromethane 1-F-1-Chloromethane	Plastics (PP,PE,PS,PVC,PA,PC,ABS,AS,PET,PVDC,UP)		6.0 1.0	
118337-09-0	12H-Dibenzo[d,g][1,3,2]dioxaphosphocin,2,4,8,10-tetrakis(1,1-dimethylethyl)-6-fluoro-12-methyl-	Plastics (PE,PP) Adhesive	Dose as necessary	6.0 6.0	0.3%
79953-85-8*	Benzamide, 3,3'-[(2-chloro-5-methyl-1,4-phenylene)bis[imino(1-acetyl-2-oxo-2,1-ethanediyl)azo]] bis[4-chloro-N-[2-(4-chlorophenoxy) -5-(trifluoromethyl)phenyl]	Plastics (PP,PE,PS,AS, ABS, PA, PET, PC,PVC,PVDC, UP) Coating	Dose as necessary		
68134-22-5	Pigment Yellow 154 2-(2-Trifluoromethylphenylazo)-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxobutanamide Same as Butanamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo-2-[[2(trifluoromethyl)phenyl]azo]]	Plastics (PE,PP, AS,PS,ABS)	It should comply with the purity of colorant		1.0%
24937-79-9	Polyvinylidene fluoride same as Ethene, 1,1-difluoro, homopolymer	paint			1.0%
25067-11-2	Perfluoroethylene propylene copolymer(Hexafluoropropene-tetrafluoroethylene copolymer)	paint		ND 0.05	
9002-84-0	Poly(tetrafluoroethylene) tetrafluoroethylene			0.05	
9010-75-7	Poly(chlorotrifluoroethylene-co-vinylidene fluoride) 26% mole vinylidene fluoride Difluoroethyelne Trichlororethylene	Rubber		5.0 QM: 0.5 mg/6 dm^4	
1187-93-5	Trifluoromethyl trifluorovinyl ether	Rubber		0.05	0.5%
90451-86-8	Perfluoroalkyl acrylate copolymer #[2]	Paper	[3]		0.5%
152521-13-6	Perfluoroalkyl acrylate copolymer #[2]	Paper	[3]		0.5%
196316-34-4	Perfluoroalkyl acrylate copolymer #[4] (Foraperle 321)[2] 2-Propenoic acid,2-methyl-, 2-(dimethylamino) ethyl ester, polymers with g-w-perfluoro-C10-16-alkyl acrylate and vinyl acetate, acetates [5]	Paper	[3]		0.5%

continued

CAS No	Name	Used in	Note	Restriction SML mg/kg	Max %
247047-61-6	Perfluoroalkyl acrylate copolymer[4] # Copolymers of 2-perfluoroalkylethyl acrylate, 2-N,N-diethylaminoethyl methacrylate, and glycidyl methacrylate	Paper	[3]		0.5%
- *	Diethanolamine single (1H,1H,2H,2H -perfluoro-alkyl) phosphate and dual-(1H,1H,2H,2H-perfluoro-alkyl) phosphate[2]	Paper	[3]		0.5%
30381-98-7	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 salt1	Paper			0.5%

Note: [1] PFSA precursors.
[2] PFCA precursors.
[3] Max.amount of usage should be calculated as in dry paper.
[4] Withdrawn from the US FDA FCN list, due to health concerns, (2012-07-06), http://www.foodmate.com/news/201207/news_2788.html
[5] http://www.ourchemical.com/catalogs_19/196316-34-4.html

Nd: Not detected
Lod: 0,01 mg/kg
*: Not on Marco's list (2012)—from list, draft
CAS No : The Chemical Abstracts Service Registry Number of the substance.
#: Removed from the list by entry of a new regulation on paper and board in 2016.

Sammenfatning

Per- og polyfluorerede forbindelser (PFAS) anvendes i fødevarekontaktmaterialer (FCM) af papir og pap for at øge materialernes barriereegenskaber over for fedt og vand. Undersøgelser har vist at stofferne har persistente, bioakkumulerende og toksiske egenskaber.

Formålet med den nordiske workshop og med denne rapport er følgende:

- skabe et overblik over brugen af PFAS i FCM af papir og pap samt bidrage til overblik over de forskellige stoffers toksicitet og deres migration til fødevarer
- give et overblik over, hvorvidt der findes risikovurderinger for fluorerede stoffer, som kan danne grundlag for specifikke regler eller anbefalinger
- give et overblik over, hvorvidt der findes analytiske metoder til analyse og kontrol af stofferne samt
- diskutere struktur og muligheder for nationale bestemmelser eller nordiske anbefalinger for PFAS i FCM af papir og pap.

Som konklusion på workshoppen blev en risikohåndtering, der reducerer det samlede indhold af organiske fluorforbindelser i fødevarekontaktmaterialer af papir og pap, anbefalet.

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PFAS IN PAPER AND BOARD FOR FOOD CONTACT

Poly- and perfluorinated alkyl substances (PFAS) are used in paper and board food contact materials (FCMs) and they have been found to be highly persistent, bioaccumulative and toxic.

The purpose of the Nordic workshop and of this report is to:

- create an overview of the use of PFAS in FCMs of paper and board and of the toxicity and migration into food of the various substances
- provide an overview of whether appropriate risk assessments for fluorinated substances exist as a basis for specific regulations or recommendations
- provide an overview of whether analytical methods suitable for analysing and regulating the substances are available
- discuss the possibility and structure of national regulations or Nordic recommendations for PFAS in FCMs of paper and board.

Risk management to reduce the total content of organically bound fluorine in paper and board FCMs is supported.

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