Nordic Council of Ministers

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NORDISKE ARBEJDSPAPIRER
NORDIC WORKING PAPERS

Analysis of per- and polyfluorinated substances in articles

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http://dx.doi.org/10.6027/NA2015-911
NA2015:911
ISSN 2311-0562

This working paper has been published with financial support from the Nordic Council of Ministers. However, the contents of this working paper do not necessarily reflect the views, policies or recommendations of the Nordic Council of Ministers.

Summary

Per- and polyfluorinated chemicals (PFAS) make up a large group of substances that have been used for decades. For the last twenty years there has been increasing focus on this group of substances as some of them have shown to be extremely persistent, bioaccumulative and toxic. There is however, a large number of per- and polyfluorinated compounds in use. For many of these substances there is very little knowledge about the health and environmental properties. In general long-chain substances are known to be more persistent.

This project is a follow up of a NORAP (Nordic Risk Assessment Project) project from 2012 where one of the main conclusions was the recognition of the limited knowledge of which perfluorinated substances are used, and in what amounts. In order to start filling some of the gaps identified in the 2012 project our aim for this study was to gather more information on the use and the incidence of per-and polyfluorinated substances in some every-day products handled by consumers. We were especially interested in analyses of the short-chained perfluorinated substances since industry has expressed a shift towards perfluorinated substances with shorter chain lengths.

Twenty-nine samples of household products were analysed for short- and long-chain per- and polyfluorinated substances at the Norwegian Institute for Air Research. All in all the findings did not reveal very high levels of per- and polyfluorinated substances in these particular products. Several of the substances were not found at all (PFHxS, 4:2 FTS, 4:2 FTOH, 6:2 PAP, 8:2 PAP, 6:2 diPAP and 8:2 diPAP). Other substances were only found a few times and then only just above the level of detection (PFBS, PFOS, 6:2 FTS, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA and PFTeA). PFOS was also only found in two products. The PFASs found the most often was 8:2 FTOH, 6:2 FTOH, PFOA, PFBA, PFHpA and PFHxA. However for the latter three the levels were mainly very low. Only PFOA, 8:2 FTOH and 6:2 FTOH were found in amounts at or above 1 µg/m^2 or 10 mg/kg or mg/L.

This project gives some information on which substances that can be detected in consumer articles. It is not possible to draw a conclusion from our results on a development in the last years towards less use of long-chain perfluorinated substances. We see in fact quite a few samples with long-chain substances. However, it does give us a picture of the levels of perfluorinated substances in certain consumer articles. A follow-up in a few years' time is certainly recommended and it would also be interesting to start to analyse samples for total organic fluorine in addition to single PFAS-substances in order to get a clearer picture of the total amounts of fluorine being used in consumer articles.

Introduction

About the PFAS substances

Per- and polyfluorinated chemicals (PFAS) make up a large group of substances that have been used increasingly since the 1950's. PFASs have been and are still being used in a great number of applications and are found in many products globally.

For the last twenty years there has been increasing focus on this group of substances, especially since it became public knowledge that there was global contamination of perfluorooctane sulfonate, PFOS (e.g. in polar bears). Being extremely persistent, having a potential for long-range transport to remote areas like the Arctic, being a reproductive toxicant and having only anthropogenic sources, PFOS is now restricted under the Stockholm convention. Another PFAS substance that has been in focus is PFOA, perfluorooctanoic acid. This substance is also persistent, bioaccumulative and toxic (PBT). There is however, a large number of other per- and polyfluorinated compounds being used. For many of these substances there is very little knowledge about the health and environmental properties and also about the use. Industry organisations claim that they are working to reduce the amount of long-chain perfluorinated substances, and rather substitute with substances with a shorter carbon back-bone, which has a lower potential to bioaccumulate. According to the U.S. EPA, companies participating in their PFOA stewardship programme have come up with 150 "replacement chemicals".[1] Yet very little is known about their potential toxicity and environmental fate. Results from blood analyses indicate an increasing exposure to short chain perfluorinated substances[2].

Known toxicological properties of PFASs

- PFOS: persistent, bioaccumulative and toxic (acute toxicity, reproductive toxicity, carcinogenicity, toxicity to organs)
- PFOA: persistent, bioaccumulative and toxic (acute toxicity, may cause eye damage, reproductive toxicity, carcinogenicity, toxicity to organs)
- PFNA: toxic (acute toxicity, may cause eye damage, reproductive toxicity, carcinogenicity, toxicity to organs)*
- C11-C14: very persistent, very bioaccumulative
- In general the long-chained PFASs are more bioaccumulative than the short-chained ones

* In accordance with the RAC opinion September 2014[3] and resulting Annex VI entry if agreed by COM

Regulatory approaches to PFASs

Although there is a vast number of PFAS substances in use globally there are only very few substances that are regulated. PFOS is the only PFAS substance that is included in a global convention, being listed under Annex B (restriction of production and use) of the Stockholm convention since 2009. Countries that have ratified the Stockholm convention must implement control measures of PFOS and related chemicals (in the EU this is regulated by the POPs regulation[4], 850/2004). An EU proposal for restriction on PFOA and PFOA precursors under the chemicals legislation REACH is currently under consideration. In addition to this PFOA and C11-C14 PFASs are listed on the REACH candidate list respectively as PBT (persistent,

[1] http://chemicalwatch.com/11013/perfluorinated-chemicals-a-persistent-problem
[2] Glynn *et al.* 2012. http://pubs.acs.org/doi/abs/10.1021/es301168c
[3] http://echa.europa.eu/opinions-of-the-committee-for-risk-assessment-on-proposals-for-harmonised-classification-and-labelling/-/substance-rev/4105/term
[4] http://ec.europa.eu/environment/pops/

bioaccumulative and toxic) and vPvB (very persistent, very bioaccumulative). In Norway there is a national ban on PFOA in consumer articles and textiles[5]. Another measure taken to reduce the risk of PFOA is the U.S. EPA voluntary agreement with the fluoropolymer industry[6]. This is a stewardship programme on PFOA, PFOA precursors, and related higher homologue chemicals. The participating companies have committed themselves to work towards a total elimination of these chemicals from emissions and in products on a global basis, no later than 2015. However, PFOA is also on Annex I to the EU directive on plastic materials and articles intended to come into contact with food[7], meaning that it is allowed to be used in food contact material. For more information on other countries' regulatory approaches to PFASs see the OECD Synthesis paper on Per- and Polyfluorinated chemicals[8].

Regulations of PFAS

- PFOS and its derivatives: Annex B of the Stockholm Convention, EUs POPs regulation. Limit: 10 mg/kg
- PFOA: National ban in Norway, in consumer articles and textiles. Limit 10 mg/kg or 1 µg/m^2
- PFOA and precursors: proposal for a restriction in EU

About this project

In 2012 the Nordic risk assessment project (NORAP) completed a survey on the use and occurrence of per- and polyfluorinated substances on the Nordic market as well as emission into the Nordic environment. The project report was published by the Nordic Chemicals Group (NKG) in the summer of 2013[9]. The report was based on literature studies and contact with industry. One of the main conclusions in the report is the recognition of the limited knowledge of which perfluorinated substances are used, and in what amounts.

This project is a follow up of the project from 2012. In order to start filling some of the gaps identified in the 2012 project our aim for this study was to gather more information on the use and the incidence of per-and polyfluorinated substances in some every-day products handled by consumers. A wide variety of products were analysed for several per- and polyfluorinated substances. Since industry has expressed a shift towards perfluorinated substances with shorter chain lengths, C4-C6, we were especially interested in analyses of such short-chained perfluorinated substances.

A similar project was also performed in 2009[10] by the Climate and Pollution Agency in Norway and we were interested to see if it was possible to find a development in the use of certain per- and polyfluorinated substances, especially to see whether the shift towards shorter chain substances is possible to pick up in this type of study.

[5] https://lovdata.no/dokument/SF/forskrift/2004-06-01-922/KAPITTEL_2
[6] http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html
[7] Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food Text with EEA relevance
[8] http://www.oecd.org/env/ehs/risk-management/PFC_FINAL-Web.pdf
[9] http://www.norden.org/no/publikasjoner/publikasjoner/2013-542
[10] Survey, screening and analyses of PFC's in consumer products. TA-2578/2009. Project report 09/47 http://www.miljodirektoratet.no/old/klif/publikasjoner/2578/ta2578.pdf

Material and methods

Choice of samples

The sampling was concentrated on a few but wide variety of household products, such as cleaning products and polishes for indoor use and for cars and sprays to waterproof shoes or clothes, food contact paper and baking forms. In addition, we included some products less commonly analysed, such as ski wax, dental floss and tablecloths. We did not include clothes, such as outdoor jackets, since other projects are focussing on such products. The sampling was done by the Norwegian Environment Agency during one day in June 2014. The samples were purchased in the vicinity of Oslo in supermarket chains that are found all over Norway, in order to select brands that are widely available on the market. The samples were then sent by mail to the laboratory (Norwegian Institute for Air Research, NILU) where they were registered, photographed and analysed.

See Table 1 below for a complete list of products together with their unique identification number. In total 29 different samples were analysed.

See annex 2 for pictures of the products.

Table 1: Samples analysed

Product / Type of article	**Store**	**Sample ID**	**Sample amount**
Table cloth 1	H. & Dysvik	1	100 cm^2
Table cloth 2, Maud Teflonduk	Kid	2	100 cm^2
Baking paper 1, Unik	Kiwi	3	100 cm^2
Baking paper 2	Meny	4	100 cm^2
Sandwich paper, Unik	Kiwi	5	100 cm^2
Cupcake forms, Unik	Kiwi	6	78.5 cm^2 (d=10)
Microwave popcorn paper 1 Eldorado (salt)	Kiwi	7A	100 cm^2
Microwave popcorn paper 2 Maarud (salt)	Kiwi	7B	100 cm^2
Car wax/polish 1 Turtle wax	Shell	8	0.05 mL
Car wax/polish 2 Autoglym	Shell	9	0.05 mL
Dishwasher liquid 1, Sun	Rema 1000	10	0.05 mL
Dishwasher liquid 2, Finish	Meny	11	0.05 mL
Waterproofing shoe treatment product 1, waterguard	XXL	12	0.05 mL
Waterproofing shoe treatment product 2, Kiwi	Rema 1000	13	0.05 mL
Waterproofing textile treatment product 1, two pack TX	XXL	14A and B	0.05 mL
Waterproofing textile treatment product 2, textile proof	G-sport	15	0.05 mL
Glider for skis 1, HF7 Violet	G-sport	16	0.02-0-04 g
Glider for skis 2, VR 55 S+LV/Fiolett	G-sport	17	0.07-0.18 g
Ski wax 1, LF6 Blue	G-sport	18	0.02-0.03 g
Lubricant for bicycles, Teflon greasetube	XXL	19	0.16 g
Dental floss 1, Easyslide	Rema 1000	20	5 meter (0.6 g)
Dental floss 2, Colgate, mint	Meny	21	5 meter (0.4 g)

Non-stick baking ware, silicon 1	Jernia	22	71.5 cm^2
Non-stick baking ware, silicon 2	Traktøren	23	0.05-0.06 g
Non-stick baking ware, cupcakes 1	Jernia	24	0.05-0.06 g
Non-stick baking ware, cupcakes 2	Traktøren	25	85 cm^2
Reusable baking liner 1	Jernia	26	100 cm^2
Reusable baking liner 2	Traktøren	27	100 cm^2

Choice of analytes

Since industry has expressed a shift towards per- and polyfluorinated substances with shorter chain lengths, C4-C6, we wanted to emphasize analyses of such short-chained substances. In the tender sent out before doing this project we therefore made a list of the short-chain substances we supposed would be found (in bold in the table below) and chose the laboratory that could best fulfil our criteria. Long-chain PFAS's were also included in the project as they turned out to be an integral part of the analysis of the laboratory. Table 2 shows which substances were included in the analyses.

Table 2: The samples were analysed for the following substances. Abbreviations are explained in annex 1. Substances in bold are considered short-chain substances.

Number of carbons	Perfluorinated carboxylic acids	Perfluorinated sulfonic acids	Fluortelomer alcohols	Polyfluoroalkyl phosphate esters	Fluortelomer sulfonates
	PFCA	PFSA	FTOH	PAPs	FTS
C4	**PFBA** CAS nr. 375-22-4	**PFBS** CAS nr. 29420-49-3 (potassium salt)			
C6	**PFHxA** CAS nr. 307-24-4	PFHxS CAS nr. 3871-99-6 (potassium salt)	**4:2 FTOH** CAS nr. 2043-47-2		**4:2 FTS** CAS nr. 757124-72-4
C7	PFHpA CAS nr. 375-85-9				
C8	PFOA CAS nr. 335-67-1	PFOS CAS nr. 1763-23-1 (sodium salt)	6:2 FTOH CAS nr. 647-42-7	6:2 diPAP CAS nr. 57677-95-9 6:2 mono-PAP CAS nr. 57678-01-0	6:2 FTS CAS nr. 29420-49-3
C9	PFNA CAS nr. 375-95-1				
C10	PFDA CAS nr. 335-76-2		8:2 FTOH CAS nr. 678-39-7	8:2 diPAP CAS nr. 678-41-1 8:2 mono-PAP CAS nr. 57678-03-2	
C11	PFUnDA CAS nr. 4234-23-5				
C12	PFDoDA CAS nr. 307-55-1				
C13	PFTrDA CAS nr. 72629-94-8				
C14	PFTeDA CAS nr. 376-06-7				

Analysis

Amount material analysed are listed in Table 1.

Ionic perfluoroalkyl substances (PFASs) and perfluoroalkyl phosphate esters (PAPs):

The samples were transferred to a 50 mL polypropylene tube, followed by addition of internal standard (25 ng) and 20 mL of methanol (lichrosolv quality). The internal standard consists of the following ionic PFAS ^{13}C labelled compounds: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFHxS, PFOS, 6;2 FTS and FOSA. In addition ^{13}C labelled compounds of the following PAPs; 6:2 monoPAP, 8:2 monoPAP, 6:2 diPAP and 8:2 diPAP were added (the abbreviations are listed in Table A1 in Annex 1). After vortexing thoroughly, the samples were put in an ultrasonic bath for 30 minutes. Afterwards the methanol was transferred to a new polypropylene tube and reduced to 2 mL. An aliquot was filtered through a polypropylene filter prior to the addition of recovery standard (brPFDA) and analysis on an UPLC-MSMS system. More details about the instrumental analysis can be found in Annex 1, see instrumental conditions, and Hanssen *et al*. (2013).

Volatile PFAS (fluorotelomer alcohol - FTOH)

The samples were transferred to a 50 mL polypropylene tube, followed by addition of internal standard (125 ng) and 20 mL of methanol (lichrosolv quality). The internal standard consists of the following volatile PFAS ^{13}C labelled compounds: 4:2 FTOH, 6:2 FTOH, 8: FTOH and 10:2 FTOH (the abbreviations are listed in Table A1 in Annex 1). After vortexing thoroughly, the samples were put in an ultrasonic bath for 30 minutes. Afterwards the methanol was transferred to a new polypropylene tube and reduced to 2 mL and centrifuged. An aliquot was taken out and recovery standard added (7:1 FTOH) prior to the analysis on a GC/MSD. More details about the instrumental analysis can be found in Annex 1.

Results

Tabular presentation of the analyses

1. Perfluorinated carboxylic acids (PFCA) - ionic PFAS

Table 3: PFCA concentrations in samples listed in Table 1. Numbers in bold are concentrations above the Norwegian national limit of 1 µg/m² for PFOA.[11] Detection limits (LOD) are listed in Table A1 in Annex 1.

		PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriA	PFTeA
µg/m²											
1	Table cloth 1	0.080	0.497	0.225	**1.91**	0.119	0.493	0.067	0.148	n.d.	n.d.
2	Table cloth 2	2.45	6.81	0.953	**6.32**	0.119	0.493	0.067	0.148	n.d.	n.d.
3	Baking paper 1	<LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
4	Baking paper 2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
5	Sandwich paper	0.103	0.434	0.106	**1.22**	0.083	0.697	0.071	0.647	0.063	0.300
6	Cupcake forms	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
7A	Popcorn paper 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
7B	Popcorn paper 2	34.5	38.9	0.648	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
µg/L											
8	Car polish 1	< LOD	< LOD	< LOD	0.470	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9	Car polish 2	< LOD	< LOD	< LOD	0.509	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
10	Dishwasher liquid 1	1.12	< LOD	< LOD	0.555	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
11	Dishwasher liquid 2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
12	Waterproofing product, shoes 1	0.752	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
13	Waterproofing product, shoes 2	< LOD	< LOD	4.62	10.8	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
14A/B	Waterproofing product, textiles 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
15	Waterproofing product, textiles 2	0.811	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
µg/kg											
16	Glider for skis 1	3.45	< LOD	7.08	92.4	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
17	Glider for skis 1	1.03	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
18	Ski wax	6.71	< LOD	1.63	0.965	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
19	Lubricant for bicycles	0.377	< LOD	1.63	56.9	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
20	Dental floss 1	< LOD	< LOD	< LOD	0.104	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
21	Dental floss 2	< LOD	< LOD	3.47	13.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
µg/m²											
22	Non-stick silicon baking ware 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
23	Non-stick silicon baking ware 2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
24	Non-stick cupcake baking ware, 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
25	Non-stick cupcake baking ware 2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
26	Reusable baking liner 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
27	Reusable baking liner 2	< LOD	< LOD	< LOD	0.268	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

[11] Results for samples 1-7B and 22-27 in ug/kg can be found in the appendix.

2. Perfluorinated sulfonic acids (PFSA) and fluortelomer sulfonates (FTS) – ionic PFAS

Table 4: PFSA and FTS concentrations in samples listed in Table 1. Concentration units are specified in the table. Detection limits are listed in table A1 Annex 1.

		PFBS	PFHxS	PFOS	4:2 FTS	6:2 FTS
µg/m²						
1	Table cloth 1	< LOD	< LOD	< LOD	< LOD	< LOD
2	Table cloth 2	< LOD	< LOD	< LOD	< LOD	< LOD
3	Baking paper 1	< LOD	< LOD	< LOD	< LOD	< LOD
4	Baking paper 2	< LOD	< LOD	< LOD	< LOD	< LOD
5	Sandwich paper	< LOD	< LOD	< LOD	< LOD	< LOD
6	Cupcake forms	< LOD	< LOD	< LOD	< LOD	< LOD
7A	Popcorn paper 1	< LOD	< LOD	< LOD	< LOD	< LOD
7B	Popcorn paper 2	< LOD	< LOD	0.239	< LOD	< LOD
µg/L						
8	Car polish 1	< LOD	< LOD	< LOD	< LOD	< LOD
9	Car polish 2	< LOD	< LOD	< LOD	< LOD	< LOD
10	Dishwasher liquid 1	< LOD	< LOD	< LOD	< LOD	< LOD
11	Dishwasher liquid 2	< LOD	< LOD	< LOD	< LOD	< LOD
12	Waterproofing product, shoes 1	< LOD	< LOD	< LOD	< LOD	< LOD
13	Waterproofing product, shoes 2	< LOD	< LOD	< LOD	< LOD	< LOD
14A/B	Waterproofing product, textiles 1	< LOD	< LOD	< LOD	< LOD	< LOD
15	Waterproofing product, textiles 2	< LOD	< LOD	< LOD	< LOD	< LOD
µg/kg						
16	Glider for skis 1	< LOD	< LOD	53.1	< LOD	< LOD
17	Glider for skis 1	< LOD	< LOD	< LOD	< LOD	< LOD
18	Ski wax	< LOD	< LOD	< LOD	< LOD	< LOD
19	Lubricant for bicycles	< LOD	< LOD	< LOD	< LOD	< LOD
20	Dental floss 1	< LOD	< LOD	< LOD	< LOD	< LOD
21	Dental floss 2	< LOD	< LOD	< LOD	< LOD	< LOD
µg/m²						
22	Non-stick silicon baking ware 1	< LOD	< LOD	< LOD	< LOD	< LOD
23	Non-stick silicon baking ware 2	< LOD	< LOD	< LOD	< LOD	< LOD
24	Non-stick cupcake baking ware, 1	0.029	< LOD	< LOD	< LOD	< LOD
25	Non-stick cupcake baking ware 2	< LOD	< LOD	< LOD	< LOD	< LOD
26	Reusable baking liner 1	< LOD	< LOD	< LOD	< LOD	< LOD
27	Reusable baking liner 2	0.019	< LOD	< LOD	< LOD	< LOD

3. Fluortelomer alcohols (FTOH) - volatile PFAS

Table 5: FTOH concentrations in samples listed in Table 1. Concentration units are specified in the table. Numbers in bold are concentrations above 0.001 weight % (10mg/kg) or 1 µg/m². Detection limits are listed in Table A1 in Annex 1.

		4:2 FTOH	6:2 FTOH	8:2 FTOH
µg/m²				
1	Table cloth 1	< LOD	**1.66**	**5.75**
2	Table cloth 2	< LOD	**129**	**366**
3	Baking paper 1	< LOD	**1.22**	**3.68**
4	Baking paper 2	< LOD	**1.37**	**3.83**
5	Sandwich paper	< LOD	**1.70**	**5.22**
6	Cupcake forms	< LOD	< LOD	**3.22**
7 A	Popcorn paper 1	< LOD	**1.14**	**3.31**
7 B	Popcorn paper 2	< LOD	**16.3**	**1.15**
mg/L				
8	Car polish 1	< LOD	0.263	3.11
9	Car polish 2	< LOD	< LOD	3.13
10	Dishwasher liquid 1	< LOD	0.391	9.29
11	Dishwasher liquid 2	< LOD	< LOD	2.62
12	Waterproofing product, shoes 1	< LOD	< LOD	0.53
13	Waterproofing product, shoes 2	< LOD	2.41	**27.7**
14 A	Waterproofing product, textiles 1	< LOD	< LOD	0.63
14 B	Waterproofing product, textiles 1	< LOD	< LOD	0.68
15	Waterproofing product, textiles 2	< LOD	**259**	0.70
mg/kg				
16	Glider for skis 1	< LOD	0.741	0.210
17	Glider for skis 1	< LOD	0.170	< LOD
18	Ski wax	< LOD	0.623	< LOD
19	Lubricant for bicycles	< LOD	0.114	< LOD
20	Dental floss 1	< LOD	0.567	2.32
21	Dental floss 2	< LOD	0.210	2.67
µg/m²				
22	Non-stick silicon baking ware 1	< LOD	**19.1**	**54.7**
23	Non-stick silicon baking ware 2	< LOD	**5.85**	< LOD
24	Non-stick cupcake baking ware, 1	< LOD	**1.40**	< LOD
25	Non-stick cupcake baking ware 2	< LOD	**16.0**	**67.4**
26	Reusable baking liner 1	< LOD	**6.53**	**18.2**
27	Reusable baking liner 2	< LOD	**76.4**	**95.2**

4. Perfluoroalkyl phosphate esters, mono-PAPs and di-PAPs

No mono and di-PAPs were detected in samples listed in Table 1.

Summary of results

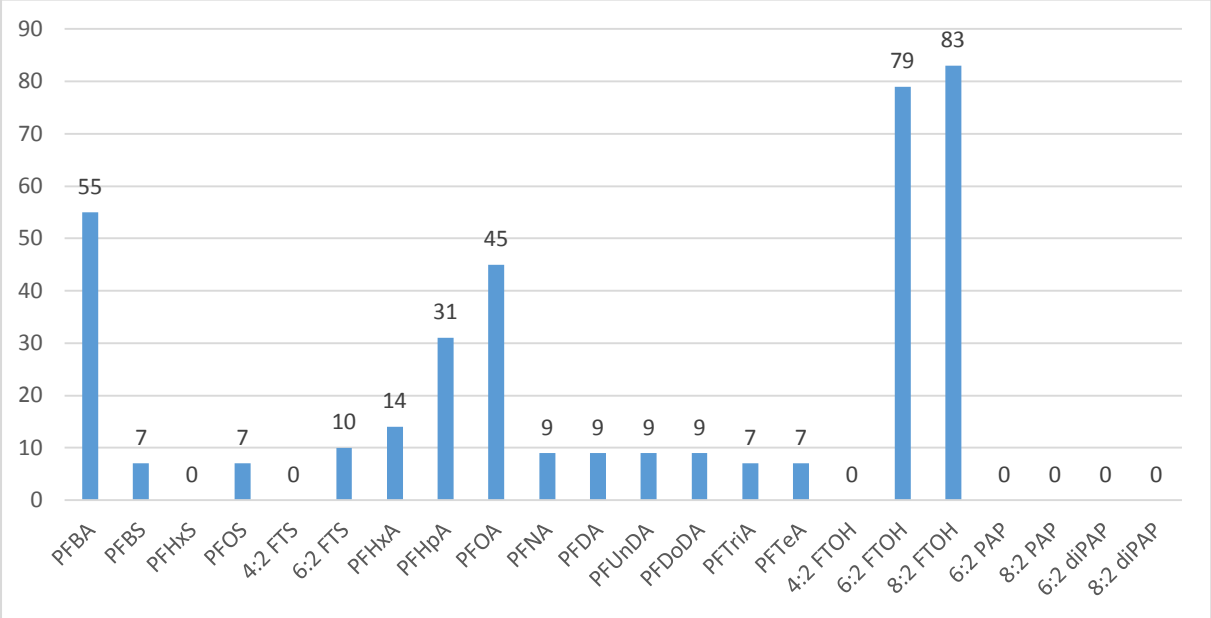

Figure 1: Percentage of samples with detected PFASs in the 29 samples.

All in all the findings did not reveal very high levels of per- and polyfluorinated substances in these particular products. Several of the substances were not found at all (PFHxS, 4:2 FTS, 4:2 FTOH, 6:2 PAP, 8:2 PAP, 6:2 diPAP and 8:2 diPAP). Quite a few substances were only found a few times and then mostly just above the level of detection (PFBS, PFOS, 6:2 FTS, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA and PFTeA). As shown in figure 1 the PFASs found the most often was 8:2 FTOH, 6:2 FTOH, PFOA, PFBA, PFHpA and PFHxA. However for the latter three the levels were mainly very low. Only PFOA, 8:2 FTOH and 6:2 FTOH were found in amounts at or above 1 µg/m^2 or 10 mg/kg or mg/L.

Related to existing regulations on PFAS, there were two findings of PFOS both well below the limits in the POPs regulation (10 mg/kg) and three findings of PFOA over the limit of 1 µg/m^2 in the Norwegian national PFOA ban in consumer articles and textiles. As the limit is still not enforceable the findings only indicate that the level found is in conflict with the regulation once the transition period is over. One of the findings is in a food contact paper, which is not regulated by the national ban.

Discussion

Levels found

Compared to the earlier project performed in 2009[8] the levels found in this project for most of the substances are overall lower. One cannot directly compare the results since the 2009 project analysed other products and brands, but comparing similar products in the two projects there seems to be a trend towards higher levels of PFAS in the products analysed in 2009 than in 2014. For instance, there were higher levels of PFOS in non-stick products in 2009 than in 2014. However, many of the samples in both projects showed no findings above the LOD, or very low levels. In addition to this, the levels found do not indicate that the use of these substances in themselves have increased or decreased. The substances analysed are "free" per- and polyfluorinated substances that may be chemical impurities or that may have broken off from the fluoropolymer, which is the actual substance used in the products. Low levels of PFASs may also indicate that the fluoropolymer used in many of the products was "cleaner", i.e. had less free substances that are available for analysis. It is however interesting to look at the percentage of findings of different substances, as illustrated in Figure 1, rather than at what level they are detected, and to see whether we can find differences between similar products in this project and the previous project.

Percentage of findings

There are some differences between the findings in this and in the previous project. Compared to the project in 2009 one can see that PFOS is detected in fewer samples in 2014. In 2009 PFOS was detected in nearly half of the samples, whereas in this project PFOS was only found in 7 percent of the samples analysed. Another finding is that PFHxS was not detected in any samples in this project, whereas it was found in approximately 35 % of the samples in the 2009. It is also interesting that PFBS also was detected in fewer samples in our project than in the 2009 project. Hence, there may be an indication that PFSAs (perfluorosulfonates) are used in fewer products now than before. There is not much difference however in the findings of PFCAs, FTOHs and FTSs between the two projects. PAPs were not a part of the previous project. We did not have any findings of PAPs in our project, which is a bit surprising since these substances have been known to be used in these kind of products, especially in food contact materials.

Conclusions and follow-up

It is not possible to draw a conclusion on whether there has been a development in the last years towards less use of long-chain perfluorinated substances and more of short-chain substances[12] from our results. We see in fact quite a few samples with long-chain substances. Of the short-chain substances that were analysed, PFBA, PFBS, PFHxA, 4:2 FTOH and 4:2 FTS, the latter two were not found at all. The first three were all detected at varying degrees and especially PFBA was quite common being found in 55 % of the samples. However, the findings are very similar to what was seen in 2009 and there is really no indication that there is a clear shift towards more use of short-chain substances.

When it comes to analysis of PFASs it is challenging to design an analytical project in a way that we can be sure that the results are useful. Firstly, the substances we analyse are not necessarily the substances being used in the articles. Secondly, we know that there are many similar substances being used in this industry, and we don't know whether the ones that we are able to

[12] Long-chain PFASs refers to PFCAs with 7 and more perfluoroalkyl carbons (such as PFNA and PFOA) and PFSAs with 6 and more perfluoroalkyl carbons (such as PFHxS and PFOS), as explained in the OECD Synthesis paper, see footnote 5.

analyse in our projects are the most relevant ones when it comes to what is being used and what is released from the treated articles or found in other sources of emissions. There is however now a rather new method that analyses total organic fluorine[13]. It would be very interesting to re-analyse the samples analysed in this project for total organic fluorine (TOF), and compare the levels we have found in this project with TOF-analyses. This may be possible in a follow-up to this study.

In sum, this project can give us an indication of what kind of substances are being used in the perfluorinated industry and it gives us a picture of the levels of perfluorinated substances in certain articles. A follow-up in a few years' time is certainly recommended and it would also be interesting to start to analyse samples for TOF in addition to single PFAS-substances in order to get a clearer picture of the total amounts of fluorine being used in consumer articles.

[13] Determination of Total Organic Fluorine (TOF) in environmental samples using flow-injection and chromatographic methods. Marek Trojanowicz, Jacek Musijowski, Mariusz Koca and Magdalena A. Dontena. Anal. Methods, 2011, 3, 1039-1045.

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- Glynn A, Berger U, Bignert A, Ullah S, Aune M, Lignell S, and Darnerud PO. 2012. Perfluorinated Alkyl Acids in Blood Serum from Primiparous Women in Sweden: Serial Sampling during Pregnancy and Nursing, And Temporal Trends 1996–2010. *Environ. Sci. Technol.*, 2012, **46** (16), 9071–9079.
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Annex 1

Abbreviations and detection limits

Table A1: PFASs abbreviations and internal standards.

Abbrevation	Full name	Detection limit
PFBA*	Perfluorobutanoic acid	0.05 µg/m^2 and µg/kg and µg/L
PFHxA*	Perfluorohexanoic acid	0.10 µg/m^2 and µg/kg and µg/L
PFHpA*	Perfluoroheptanoic acid	0.06 µg/m^2 and µg/kg and µg/L
PFOA*	Perfluorooctanoic acid	0.06 µg/m^2 and µg/kg and µg/L
PFNA*	Perfluorononanoic acid	0.15 µg/m^2 0.08 µg/kg and µg/L
PFDA*	Perfluorodecanoic acid	0.15 µg/m^2 0.08 µg/kg and µg/L
PFUnDA*	Perfluoroundecanoic acid	0.15 µg/m^2 0.08 µg/kg and µg/L
PFDoDA*	Perfluorododecanoic acid	0.09 µg/m^2 0.05 µg/kg and µg/L
PFTriA	perfluorotridecanoic acid	0.05 µg/m^2 and µg/kg and µg/L
PFTeDA*	Perfluorotetradecanoic acid	0.09 µg/m^2 and µg/kg and µg/L
PFBS	Perfluoro butane sulfonic acid	0.10 µg/m^2 and µg/kg and µg/L
PFHxS*	Perfluorohexane sulfonic acid	0.10 µg/m^2 and µg/kg and µg/L
PFHpS	Perfluoroheptane sulfonic acid	
PFOS*	Perfluorooctane sulfonic acid	0.10 µg/m^2 and µg/kg and µg/L
FOSA*	Perfluorooctane sulfonamide	
4:2 FTS	4:2 Fluorotelomer sulfonic acid	0.03 µg/m^2 and µg/kg and µg/L
6:2 FTS*	6:2 Fluorotelomer sulfonic acid	0.03 µg/m^2 and µg/kg and µg/L
brPFDA	3,7-dimethyl perfluorooctanoic acid (branched perfluorodecanoic acid)	
6:2 monoPAP*	6:2 Perfluoroalkyl phosphate monoester	Only qualitative determination
8:2 monoPAP*	8:2 Perfluoroalkyl phosphate monoester	Only qualitative determination
6:2 diPAP*	6:2 Perfluoroalkyl phosphate diester	Only qualitative determination
8:2 diPAP*	8:2 Perfluoroalkyl phosphate diester	Only qualitative determination
4:2 FTOH*	4:2 Fluorotelomer alcohol	0.01 µg/m^2 0.0001 µg/kg and µg/L
6:2 FTOH*	6:2 Fluorotelomer alcohol	0.01 µg/m^2 0.0001 µg/kg and µg/L
8:2 FTOH*	8:2 Fluorotelomer alcohol	0.1 µg/m^2 0.001 µg/kg and µg/L

*Also as ^{13}C labelled ISTD

Quality assurance

Ionic PFASs:

The extraction method applied only allows for the determination of the extractable PFAS. All PFAS chemically bound to a fluoropolymer are not accessible for the applied method. Using ^{13}C labelled internal standards for as many PFAS congeners as possible allows for a control of potential suppression of the analytical signal caused by matrix. Therefore, NILU uses a total of 14 ^{13}C labelled internal standards for the ionic PFAS (see table A1), which were added to the sample. We find the method applicable for these types of samples. To further validate the method, a certified reference material or a laboratory comparison test is part of PFAS analyses in general. However, for textiles or food packing materiel no such material is available. To compensate for that, the recovery of the 14 ^{13}C labelled internal standards was used as an additional quality measure. The recovery differed between sample materials and varied from 24 to 130 %. Finally, blank controls give insight into eventual contamination in the laboratory. Four blank samples were run together with the samples. None of the investigated PFASs were detected in blank samples.
The limit of detection was determined by using three times the noise of the mass transition of each PFAS in every sample. The LODs are presented together with the results in Table A1.

To give insight into the variations of the chemical analyses as well as the inhomogeneous distribution of PFAS, three replicates of one textile sample were analysed. The textile sample was a jacket, not a part of this project but included here for illustration. The sample chosen from the jacket was fabric uniform in texture and colour. Detectable PFAS concentrations of a broad variety were found as well as slightly exceeding of the PFOA threshold. The results are presented in Table A2.

Table A2: Three analysed replicates of a textile sample. Concentrations in µg/m^2.

	Parallel 1	Parallel 2	Parallel 3	Average	Stdev	% RSD
4:2 FTS	<0.10	<0.10	<0.10	-	-	-
6:2 FTS	<0.10	<0.10	<0.10	-	-	-
8:2 FTS	<0.15	<0.15	<0.15	-	-	-
PFBS	<0.03	<0.03	<0.03	-	-	-
PFHxS	<0.15	<0.15	<0.15	-	-	-
PFHpS	<0.15	<0.15	<0.15	-	-	-
PFOS	<0.15	<0.15	<0.15	-	-	-
PFDcS	<0.30	<0.30	<0.30	-	-	-
FOSA	<0.15	<0.15	<0.15	-	-	-
PFHxA	<0.90	<0.90	<0.90	-	-	-
PFHpA	0.15	0.15	0.15	0.15	0.003	1.8
PFOA	1.08	1.07	1.10	1.09	0.02	1.1
PFNA	1.22	1.38	1.38	1.33	0.09	7.0
PFDA	0.84	0.83	0.82	0.83	0.01	1.1
PFUnDA	0.60	0.54	0.57	0.57	0.03	4.9
PFDoDA	0.63	0.63	0.64	0.64	0.01	0.9
PFTrDA	0.29	0.55	0.57	0.47	0.16	33
PFTeDA	0.24	0.28	0.27	0.26	0.02	8.5

RSD: relative standard deviation

In general terms, an analytical method with uncertainties below 20% is accepted. As shown in Table A2, the method applied by NILU results in relative standard deviations ranging between 0.9 and 8.5%, with the exception of PFTrDA where the RSD was 33%, which is well below the

accepted uncertainty. The increased uncertainty for PFTrDA could be explained by low concentrations and no ^{13}C labelled internal standard.

In the standard method (see "Instrumental conditions; Analysis of ionic PFASs") there is only one transition for the PFBA, whereas for the other PFASs we have two. To verify the concentration of this compound the samples were reanalysed on a different column with a different solvent system (see instrumental conditions below), instrumental settings on the MS analyser is described in Hanssen *et al.* (2013). The PFBA concentration is reported for the samples where the calculated concentration in the two system was similar.

Volatile PFAS:

There have been no replicate extraction of textiles to evaluate the distribution of volatile PFASs. No reference material exist for this purpose either. For 8:2 FTOH there was a blank contamination which resulted in higher LOD.

PAPs:

In this investigation, we chose to add ^{13}C labelled internal standard for the analytes even though the results were to be reported as qualitative and not quantitative. The method used for extraction was the standard extraction method used in the laboratory with minor modifications, such as no suspensive clean up to avoid losing the analytes which are very surface active. Despite this, we were not able to detect the internal standard for the mono PAPs, only for the di-PAPs.

Instrumental conditions

Analysis of the volatile FTOH

FTOHs were analysed by gas chromatography mass-spectrometry (GC–MS) in selected ion monitoring (SIM) mode. An Agilent 7890A GC with split/splitless injector coupled to a 5975C MSD (Agilent, Böblingen, Germany) was used with helium carrier gas flow rate of 0.8 mL/min, and methane as reagent gas in positive chemical ionization (PCI) mode for quantification. Injection volume was 1 µL, constant injector temperature was set to 200 °C in splitless mode. The chromatographic analysis was performed on a Supelcowax 10 column (30 m × 0.25 mmi.d.×0.25 µm film). The GC temperature program incorporated an initial temperature of 50 °C with a hold time of 1 min, increased by 3 °C/min to 70 °C, followed by a second temperature ramp of 20 °C/min to 220 °C held for 4 min, and followed by a third temperature ramp of 120 °C/min to 275 °C held for 5 min. Two masses were monitored for each analyte, see Table A3.

Table A3: Quantifier and qualifier mass used for FTOH qualtification.

Analyte	Quantifier mass (m/z)	Qualifier mass (m/z)
13C 4:2 FTOH	269.1	231
13C 6:2 FTOH	369.1	331
13C 8:2 FTOH	469.1	431
4:2 FTOH	265.1	227
6:2 FTOH	365.1	327
8:2 FOTH	465.1	437
7:1 FTOH	401	381

Analysis of the ionic PFASs

Chromatographic conditions (as described in Hanssen et al, 2013); PFASs were analyzed by ultrahigh pressure liquid chromatography triple–quadrupole mass-spectrometry (UHPLC-MS/MS). Analysis was performed on a Thermo Scientific quaternary Accela 1250 pump (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a PAL Sample Manager (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to a Thermo Scientific Vantage MS/MS (Vantage TSQ) (Thermo Fisher Scientific Inc., Waltham, MA, USA); 10 µL was injected on a Waters Acquity UPLC HSS 3 T column (2.1× 100 mm, 1,8 µm) (Waters Corporation, Milford, MA, USA) equipped with a Waters Van guard HSS T3 guard column (2.1× 5 mm, 1.8 µm) (Waters Corporation, Milford, MA, USA). Separation was achieved using 2 mM NH4OAc in 90:10 methanol/water (A) and 2 mM NH4OAc in methanol (B) as the mobile phases. In order to distinguish the perfluoroalkyl carboxylic acids (PFCAs) leaching from the pump and the degasser from that originating from a sample, a Waters XBridge C18 column (2.1× 50 mm, 5 µm) (Waters Corporation, Milford, MA, USA) was installed after the pump and before the injector. An overview of parent ions, monitored transitions, S-lens conditions and collision energies for the UHPLC-MS/MS is available in Hanssen et al 2013.

Analysis of the mono and di-PAPs

Similar chromatographic conditions as for the ionic PFASs (Hanssen *et al*., 2013). Ionisation was conducted in the negative electrospray ionisation mode (ESI-) with the following conditions: spray voltage was kept at -2000 V, vaporizer temperature 350 °C, sheat gas pressure at 30 au, ion sweep gas pressure of 1.0 au and aux valve flow at 10 au. The MS was run in SRM mode with a capillary temperature of 180 °C, chrom filter peak width 5 sec, collision gas pressure 1.5 mTorr, Q1 and Q3 peak width of 0.7 Da and a cycle time of 0.4 sec. Declustering voltage was set to 10. Details about the analytical conditions, the parent ions, monitored transitions, collision energies and S-lens settings are provided in Table A4.

Table A4: Overview of parent ions, monitored transitions, S-lens conditions and collision energies for the UHPLC-MS/MS. Q1 is the quantifier ion, and Q2 the qualifier ion.

Analyte	Parent ion (m/z)	Transition 1 (m/z) (Q1)	Transition 2 (m/z) (Q2)	Collision energy (V)	S-lens (V)
6:2 mono PAP	443	97	79	16	89
8:2 mono PAP	543	97	79	10	89
6:2 di PAP	789	97	443	20	153
8:2 di PAP	989	97	543	10	229

Additional analysis of PFBA

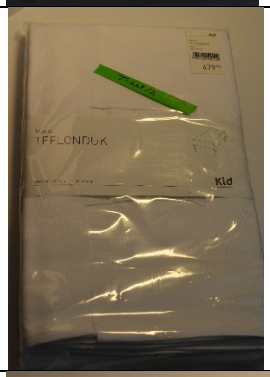
Extracts (10 µL) were injected onto an Ascentis Express F5 PFP Column (2.7 µm, 10 cm×2.1 mm, Sigma–Aldrich) equipped with an Ascentis Express F5 PFP guard column (2.7 µm, 5.0 mm×2.1 mm), both maintained at 30°C. The mobile phase consisted of 20 mM ammonium formate/20 mM formic acid in water (solvent A) and MeOH with 20 mM ammonium formate/20 mM formic acid (solvent B) maintained at a 250 µL/min flow rate. Gradient conditions were: 90% A for 1 min, 40% A by 4 min, 12% A by 16.3 min, 0% A by 16.8 min and then 90% A and allow equilibration for 3.5 min.

PFAS results in µg/kg.

Table A5: Ionic PFAS concentrations (µg/kg) for sample 1-7B and sample 22-27.

Sample ID	PFBA	PFBS	PFHxS	PFOS	4:2 FTS	6:2 FTS	PFHxA	PFHpA	PFOA
1	0.359	<0.10	<0.10	<0.10	<0.03	<0.03	2.23	1.01	8.57
2	12.4	<0.10	<0.10	<0.10	<0.03	<0.03	34.5	4.83	32.0
3	<0.05	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
4	0.049	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
5	2.69	<0.10	<0.10	<0.10	<0.03	<0.03	11.31	2.76	31.7
6	0.031	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
7A	0.048	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
7B	319	<0.10	<0.10	2.21	<0.03	<0.03	359	5.98	0.08
22	<0.05	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
23	1.66	<0.10	<0.10	<0.10	<0.03	0.052	<0.10	<0.06	0.944
24	<0.05	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
25	<0.05	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
26	<0.05	<0.10	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	<0.06
27	<0.05	0.034	<0.10	<0.10	<0.03	<0.03	<0.10	<0.06	0.491

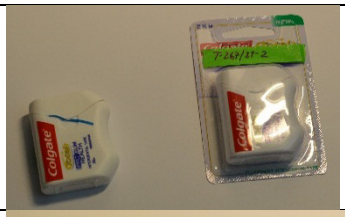
Annex 2, pictures of analysed samples

Sample ID	Product	Product / Type of article
1		Table cloth 1
2		Table cloth 2, Maud Teflonduk
3		Baking paper 1, Unik
4		Baking paper 2, Toppits
5		Sandwich paper, Unik
6		Cupcake forms, Unik

7A		Microwave popcorn paper 1 Eldorado (salt)
7B		Microwave popcorn paper 2 Maarud (salt)
8		Car wax/polish 1 Turtle wax
9		Car wax/polish 2 Autoglym
10		Dishwasher liquid 1, Sun

11		Dishwasher liquid 2, Finish
12		Waterproofing shoe treatment product 1, Waterguard
13		Waterproofing shoe treatment product 2, Kiwi
14A and B	 	Waterproofing textile treatment product 1, Nikwax two pack TX

15		Waterproofing textile treatment product 2, textile proof, Toko
16		Glider for skis 1, Swix HF7 Violet
17		Ski wax, Swix VR 55 S+LV/Fiolett
18		Glider 1, Swix LF6 Blue
19		Lubricant for bicycles, TF2 Teflon greasetube
20		Dental floss 1, Jordan Easyslide

21		Dental floss 2, Colgate, mint
22		Non-stick baking ware, silicon 1, Invite
23		Non-stick baking ware, silicon 2, Patisse
24		Non-stick baking ware, cupcakes 1, Invite
25		Non-stick baking ware, cupcakes 2, Patisse
26		Reusable baking liner 1, Invite

27		Reusable baking liner 2