

PILOT SCREENING OF PERLUOROALKYL SUBSTANCES (PFASs) IN CONSUMER PRODUCTS FROM SPANISH MARKETS: PRELIMINARY RESULTS

Sánchez AI¹, Roscales JL¹, Muñoz-Arnanz J¹, Jiménez B¹

¹Dept. of Instrumental Analysis and Environmental Chemistry, Institute of General Organic Chemistry, CSIC (IQOG-CSIC). Madrid, Spain, 28006, bjimenez@iqog.csic.es

Introduction

Poly- and perfluoroalkyl substances (PFASs) are widely distributed emerging anthropogenic pollutants¹ that currently include some chemicals considered as Persistent Organic Pollutants (POPs). Physicochemical characteristics of these chemicals provide, among other important properties, both oil and water repellency that results in an ample range of applications in consumer products²⁻⁵. Well-known applications of PFASs include textile, non-stick ware, paper, carpets and firefighting agents. However, the range of applications can be widely extended including waterproof agents, lubricants, paints as well as electric and electronic devices.

Most studies have focused on perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonates (PFASs) mainly because their POP-like properties⁶. Particularly, perfluorooctane sulfonate (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) have been included in Annex B of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) since 2009⁶. Regarding PFCAs, perfluorooctanoic acid (PFOA), its salts and related compounds are currently listed as candidate substances. Although important efforts have been made since the 2000s by governments and manufacturers to reduce or eliminate PFOS and PFOA, China and other developing Asian countries have increased their PFAS production and emissions since the early 2000s⁷. Moreover, regulations of PFASs have led to the production and use of alternative fluorinated compounds such as short-chain PFASs and semi-fluorinated compounds⁸.

According to the decision SC-8/18, members of the SC are encouraged to explore and communicate the potential presence of PFOS and related compounds in consumer products. For that, the SC has prepared the “Draft Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles”. Following these recommendations, here we aimed to present some preliminary results on the presence of PFOS and PFOA in consumer products acquired in the Spanish market. Additional related compounds including short and other long-chain PFASs and PFCAs were also evaluated. To our knowledge, this is the first attempt to assess the presence of PFASs in a wide range of consumer products from different categories available in the Spanish market. Therefore, our results can provide crucial knowledge to develop an efficient strategy for screening of PFASs at national scale.

Materials and methods

Sampling strategy: Consumer products were chosen based on the probability of containing PFASs. Products with water/lipid repellent properties or with fluorine materials in their composition (e.g. Teflon®) were prioritized. Among the available options, products selected for sampling were those whose PFAS content was identified in previous studies^{2-5,9}, and were also widely consumed. For all products fabrication origin was determined. Under these considerations a total of 19 products were selected, including textiles with different uses, non-stick ware, carpets, paper materials, and were purchased in common malls with high consumer demand from the state capital, Madrid.

PFAS determination: Textile and paper sample treatment and extraction followed that described in Van der Veen et al. 2016² with minor modifications. Briefly, a portion of 10 cm² was cut with methanol pre-cleaned stainless steel scissors. Subsamples were weighted and thoroughly cut into tiny pieces for homogenization. In the case of kitchenware spatulas the material was cut and grinded using liquid nitrogen and 2 g were weighted for its analysis. All subsamples were placed into methanol pre-cleaned polypropylene (PP) Falcon tubes (Deltalab, Barcelona, Spain) and 20 µL of a surrogate solution containing (¹³C, ¹⁸O)-labelled PFASs (Wellington Laboratories, Ontario, Canada) at 50 pg/µL were added (Table 1). Then successive extractions using ~5 mL of methanol (SupraSolv® Merk, Darmstadt, Germany) and applying vortex-mixing (2 min) and shaker plate (30 min) were applied. After centrifugation methanol was transferred into clean PP tubes and concentrated under a gentle stream of N₂ to ~0.5 mL. Subsequent clean up has been described elsewhere³. Basically, the concentrated extracts were transferred to PP eppendorfs together with 25 mg of ENVI-Carb (Supelco, Bellefonte, USA) to which 50 µL of glacial acetic acid (HPLC grade, Scharlab, Sentmenat, Spain) was added. Eppendorfs were tightly capped and vortex-mixed thoroughly before centrifuging (10,000 rpm for 10 min). Supernatant extracts were transferred to auto-filter PP vials (syringeless filter device Mini-UniPrep™, Whatman, Buckinghamshire, UK), dried under a gentle N₂ stream and reconstituted with 200 µL of the injection standard solution including ¹³C₈-

PFOA, ¹³C₈-PFOS, D₃-N-MeFOSA and ¹³C₇-PFUDA (Wellington laboratories) at 5 pg/μL in 30:70 water:methanol (LiChrosolv®:SupraSolv®, Merck).

In the case of frying pans, the extraction and purification method has been previously detailed in Sinclair et al. 2007¹⁰. Briefly, 250 mL of water (LiChrosolv®, Merck) previously spiked with labelled PFAS surrogates were boiled in pans two times for 10 min. Water extracts were collected in PP 1 liter bottles and then passed through solid phase extraction (SPE) cartridges (STRATA™ reversed polymeric phase 3 μm, Phenomenex) previously eluted with 4 mL of 0.1% NH₄OH in methanol, 4 mL MeOH and 4 mL H₂O. After water samples were passed through the SPE cartridges using a Baker® vacuum station they were dried and eluted with 4 mL of 0.1% NH₄OH in methanol. Methanol was transferred to vials as previously described for the other types of samples.

Identification and quantification of 15 ionic PFASs (five PFASs -C_{4,6,8,10,12}- and ten PFCAs -C₄₋₁₃-) was performed using a Waters Acquity Ultra Performance Liquid Chromatography system coupled with a Waters XEVO TQS, triple-quadrupole mass spectrometer (UPLC-MS/MS) operating in the multiple-reaction-monitoring (MRM) mode and equipped with an electrospray ionization (ESI) source (Waters, Milford, MA, USA). Extracts were injected (10 μL) onto an Acquity UPLC BEH C18 column (1.7 μm, 2.1 × 50 mm; Waters). Separation was achieved using a gradient mobile phase of water and methanol with a constant 1% of acetonitrile buffer at a flow rate of 400 μL/min. Injection and instrumental conditions, as well as MS/MS parameters for the target compounds followed those described in González-Gaya et al. 2014¹ with some modifications¹¹. Quantification was based on a linear ten point calibration curve using the isotopic dilution technique.

Quality Assurance and Quality Control (QA/QC): Fluorinated materials were avoided in the laboratory, using exclusively PP materials thoroughly cleaned with methanol (SupraSolv® Merck). Blank samples covering the whole analytical procedure were included for all consumer product categories. In those cases in which blanks showed analyte concentrations above the Limit of Quantification (LOQ) they were subtracted in the corresponding sample batch. Limits of detection (LOD) and quantification were calculated as 3 and 10 times respectively the signal to noise ratio. Depending on the sample, LOD varied from 0.02 to 0.10 pg/μL for PFOS and from 0.01 to 0.04 for PFOA. Target compounds were identified based on similar retention times and a ratio between the monitored ions of ± 30% of the mean values obtained for calibration standards. Satisfactory results were found for labelled PFOS and PFOA and for most examined compounds (Table 1). Concentrations of native target compounds are recovery corrected by the isotopic dilution technique. Our lab has recently participated in an inter-laboratory assessment of PFAS (POPs IL4, UNEP) with satisfactory z-score results for all PFAS studied here.

Table 1. Mean ± standard deviation recovery (%) of labelled PFASs in the studied samples categories.

Labelled PFAS	Textiles	Kitchenware and papers	Frying pans	Total
PFBA- ¹³ C ₄	78±35	87±30	2±1	72±41
PFHxA- ¹³ C ₂	89±27	88±20	88±0	89±24
PFOA- ¹³ C ₄	75±14	83±15	89±2	79±15
PFNA- ¹³ C ₅	57±25	73±13	105±10	66±27
PFDA- ¹³ C ₂	116±77	144±66	139±13	126±73
PFUnDA- ¹³ C ₂	74±29	97±23	72±24	80±29
PFDoDA- ¹³ C ₂	44±26	55±38	33±22	46±30
PFHxS- ¹⁸ O ₂	198±213	114±48	134±23	169±180
PFOS- ¹³ C ₄	77±18	80±16	91±7	80±18

Results and discussion

PFOA was detected in almost all studied products, while PFOS was only found above the LOD in four of them: carpet, mountain jacket, sofa cover and one of the studied frying pans (Table 2). Moreover, with the exception of the carpet when both PFAS were detected, PFOA was found at greater concentrations. These differences between PFOS and PFOA presence could be related to the earlier and more global regulation of PFOS compared to PFOA¹².

According to the European Union (EU) current legislation on PFOS (EU Regulation N°757/2010)¹³, it is established a threshold level of 1 μg/m² for textiles and surface treated materials and a limit below 0.1% of weight (1 g/kg) for articles and manufactured products. PFOS concentrations found in Spanish textiles were at least two orders of magnitude below the legal limit. Similarly, non-stick products (weight of pans ~570g) showed PFOS concentrations several orders of magnitude below those authorized in the regulation. Although our results fall within the range of concentrations previously reported in other European studies, greater levels have been

reported in several cases. A pilot study in Norway³ reported PFOS concentrations ranging from ND to 38.0 µg/m² (mean 1.04) in textiles and coated materials following the next concentration pattern: food contact paper < casual clothes < carpets < technical mountain clothes < leather. Also, non-stick ware from Norwegian markets ranged from ND to 60 ng/g. Kothhoff et al. (2015)⁵ reported median concentrations ranging from 1.0 to 9.0 µg/m² increasing according to coated paper < awning cloth < leather < outdoor cloth. Other researchs on frying pans using a similar method to determine PFOS presence did not reported significant concentrations of this chemical¹⁰. Finally, previous studies in packing materials purchased in Spain⁹ including microwave popcorn bags and food contact papers, also reported PFOS concentrations below the LODs.

Table 2. PFOS and PFOA concentrations in the examined products. Note that measurement units vary depending on the product and the analytical method. When possible different units are reported for comparative purposes.

Code	Textiles and coated fabrics	PFOA (µg/m ²)	PFOS (µg/m ²)	PFOA (ng/g)	PFOS (ng/g)
1	Carpet	0.050	0.078	0.040	0.063
2	Suit shirt (100% cotton)	0.005	<LOD	0.053	<LOD
3	T-shirt (polyamide)	0.007	ND	0.029	ND
4	Trouser suit	0.011	<LOD	0.056	<LOD
5	Working clothes (stain-resistant)	0.061	<LOD	0.339	<LOD
6	School uniform (stain-resistant)	0.022	<LOD	0.091	<LOD
7	Waterproof mountain jacket	0.020	0.034	0.078	0.131
8	Faux-leather jacket	0.072	ND	0.176	ND
9	Mountain waterproof boots	0.077	0.021	-	-
10	Silicone based tablecloth	0.029	<LOD	0.290	<LOD
11	Elastic sofa cover	ND	0.046	ND	0.125
12	Umbrella	0.062	ND	0.892	ND
	Non-stick kitchenware and paper materials			PFOA (ng/g)	PFOS (ng/g)
13	Microwave popcorns bags			0.102	ND
14	Microwave popcorns bags (with butter)			0.079	ND
15	Oven paper			0.187	ND
16	Silicone spatula			0.014	<LOD
17	Nylon spatula			0.004	ND
				PFOA (ng)	PFOS (ng)
18	Frying pan (<i>Teflon</i> ®)			0.40	<LOD
19	Frying pan (low price)			0.956	0.027

ND = not detected

PFOA concentrations strongly varied among the studied products (Table 2). Greater concentrations tended to occur in non-stick frying pans and coated food-contact papers, although comparable concentrations were found in some textiles such as stain-resistant and faux-leather clothes. PFOA concentrations found in this study agree well with those previously reported in European studies. Herzke et al. (2012)³ reported a concentration range of ND-3.74 (mean 0.65) µg/m² in coated fabrics including textiles and food contact papers and concentrations below LODs in non-stick ware and frying pans with the exception of one studied pan (436 ng/g). Median concentrations in German products⁵ were 1.1, 3.2, 5.8, 6.0 and 12.4 µg/m² in carpet, coated food-contact paper, awning cloth, outdoor textile and leather, respectively. In both studies maximum concentrations were reported in non-stick ware or coated food contact paper. Zabaleta et al. (2016)⁹ reviewed PFOA concentrations reported in packaging materials including food-contact papers. In comparison, our results on popcorn microwave cooking bags and oven paper are within the concentration range reported previously in Spain in 2016 and in concert or clearly below those reported in other European and worldwide studies conducted before. Finally, similar studies on frying pans (n=7) have reported PFOA levels¹⁰ below 2.5 ng, analogous to those reported here, with single exceptions that reach 7.0 and 75 ng.

Regarding the remaining studied PFAS (Figure 1), our results must be taken with caution. Although recoveries for most PFAS were highly satisfactory in most cases, some unsatisfactory results (recovery >150 or <50%) were found. Basically, recovery of PFBA in frying pans was extremely low, probably due to volatilization because of the boiling process during extraction. In contrast, high recovery values were obtained for labelled PFHxS in the school uniform, the mountain jacket and the nylon spatula; and for PFDA in the tablecloth, faux-leather jacket, school uniform and nylon spatula (Table 1). However, none of these compounds was detected in the products that showed unsatisfactory recoveries, which make us confident about PFAS profiles presented here.

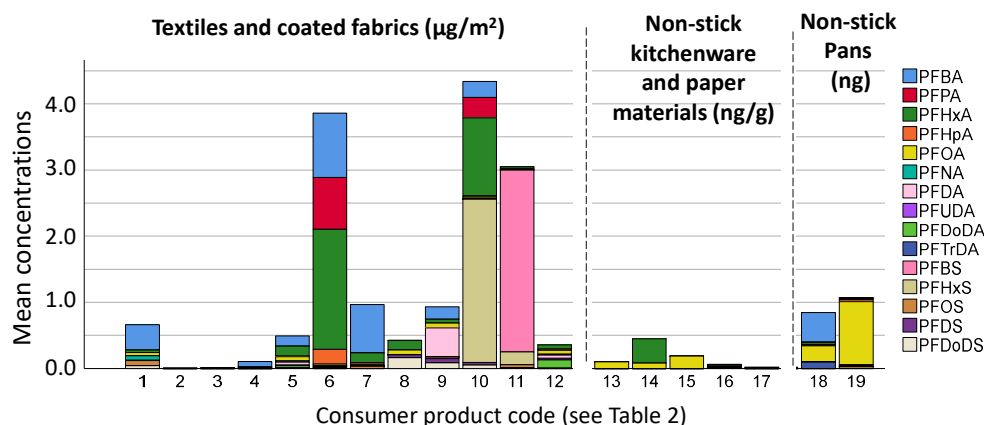


Figure 1. Concentrations of PFASs in consumer products from Spanish market.

Among the PFASs studied here, short chain PFCAs and PFSAs tended to show the greatest concentrations in most textiles studied (Figure 1). Nonetheless, total amounts of PFASs in most samples were below the threshold level ($1 \mu\text{g}/\text{m}^2$) established for PFOS alone, which indicates that concentrations can be considered generally low. Three exceptions to this general pattern due to great concentration of PFAS could be observed. Markedly greater concentrations of short-chain PFCAs were found in the school uniform (sample 6; total $C_{4-7} = 3.76 \mu\text{g}/\text{m}^2$) and the tablecloth (sample 10; total $C_{4-7} = 1.74 \mu\text{g}/\text{m}^2$). Moreover, the last one showed the greatest concentrations of PFHxS ($2.47 \mu\text{g}/\text{m}^2$) reported here, although the elastic sofa cover was the sample that showed the greatest total amount of short-chain PFSAs (PFBS $2.74 \mu\text{g}/\text{m}^2$, PFHxS $0.20 \mu\text{g}/\text{m}^2$). Previous studies on similar consumer products in Europe also have commonly found greater concentrations for short-chain compounds compared to other PFAS, and in the same order of magnitude compared to those reported here³⁻⁵. Opposite to textiles, in non-stick products PFOA tended to be the prevalent compound, also in agreement with previous studies^{9,10}.

Although the limited number of samples studied here does not allow outlining general certain conclusions, our results do not suggest that application of PFAS in products acquired in Spain exceed the threshold levels established in the European legislation. However, our results indicate that short-chain PFAS are relatively abundant in consumer products and probably are being applied as alternatives to PFOS and/or PFOA. This study settles a good starting point to improve both, the analytical approach and the representability of future PFAS screening studies in consumer products at national level in Spain.

Acknowledgements

Authors thank the Spanish Ministry for the Ecological Transition for founding (Project 15CAES004) the current study. We also thank Sagrario Calvarro for her invaluable support during PFAS determination.

References

- González-Gaya B, Dachs J, Roscales J L, Caballero G, Jiménez B. (2014). *Environ. Sci. Tech.* 48(22): 13076-13084.
- Van der Veen I, Weiss JM, Hanning AC, de Boer J, Leonards PEG. (2016). *Talanta* 147: 8-15.
- Herzke D, Olsson E, Posner S. (2012) *Chemosphere* 88(8): 980-987.
- Liu X, Guo Z, Krebs KA, Pope RH, Roache NF. (2014) *Chemosphere* 98: 51-57.
- Kotthoff M, Müller J, Jüriling H, Schlummer M, Fiedler D (2015) *Pollut. Res.* 22(19): 14546-14559.
- Stockholm Convention (2009). C.N.524.2009.TREATIES-4 (Depositary Notification).
- Xie S, Wang T, Liu S, Jones KC, Sweetman AJ, Lu Y. (2013) *Environ.Int.* 52: 1-8.
- Wang Z, Cousins IT, Scheringer M, Hungerbühler K. (2013) *Environ. Int.* 60: 242-248
- Zabaleta I, Bizkarguenaga E, Bilbao D, Etxebarria N, Prieto A, Zuloaga O. (2016) *Talanta* 152: 353-363
- Sinclair E, Kim SK, Akinleye HB, Kannan K. (2007). *Environ.Sci.Tech.* 41(4): 1180-1185.
- Roscales JL, Vicente A, González-Solís J, Ryan P, Jiménez B. (2019) *Environ.Sci.Tech.* Under 2nd revisión.
- Ahrens L, Bundschuh M. (2014) *Environ.Toxicol.Chem.* 33(9): 1921-1929.
- European Union (UE). Commission Regulation N° 757/2010, OJ L223, 25th August 2010, pages 29-36.