CONffIDENCE: Contaminants in food and feed: Inexpensive detection for control of exposure

Analysis of Perfluorinated Compounds in Fish: a comparision between farm and open sea fish

Marta Llorca[1], Marinella Farré[1,+], Jan Poustka[2], Petra Hradkova[2], Jana Pulkrabova[2], Jana Hajslova[2], Damià Barceló[1,3,4]

[1]Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain;
[2] Institute of Chemical Technology Prague, VSCHT
[3] Catalan Institute for Water Research, ICRA, Girona, Spain
[4] King Saud University, Riyadh, Saudi Arabia
[+]e-mail contact: mfuqam@cid.csic.es

WP1b: Pefluorinated Compounds (PFCs)

I) Introduction:

PFCs comprise a large group of compounds widely used in industrial applications since 40s. They have unique properties to make materials stain, oil, and water resistant, and are widely used in several applications such as stain and water resistant textiles, food packaging, in fire extinguishing formulations, pesticides, paints, personal care products and surfactant agents, among others. PFCs are resistant to breakdown, ubiquitous environmental contaminants, which persist and may be accumulated attached to proteins and biomagnified through the food chain. In recent years, an increasing scientific interest has raised due to their widespread distribution. The main direct routes of exposure of PFCs to humans are in their diet and drinking water. Although fish is one of the main sources of PFCs in diet [1].

This work presents the study of three selected PFCs (Table 1). The analyzed samples corresponded to three different species from different markets in Barcelona: salmon, turbot and gilthead bream. The samples were from two origins (Figure 1): I) farm fish (n = 9) and, II) open sea fish (n = 9). A total of 54 samples were analyzed in triplicate.

Cantabric Sea (Open sea fish)

Mediterranean Sea (farm fish)

Figure 1: Open sea and farm fish from different regions.

Table 1: Analytical compounds

Analyte	Surrogate	Internal Standard
Perfluorooctanoic acid (PFOA)	[$^{13}C_4$]-Perfluorooctanoic acid (MPFOA ($^{13}C_4$))	[1,2-$^{13}C_2$]-Perfluorooctanoic acid (MPFOA ($^{13}C_2$))
Perfluorooctanesulfonate ion(PFOS)	Ion [$^{13}C_4$]-Perfluorooctanesulfonate (MPFOS ($^{13}C_4$))	Ion [$^{13}C_8$]-Perfluorooctanesulfonate (M8PFOS ($^{13}C_8$))
Perfluorooctanesulfonamide (FOSA)	[$^{13}C_8$]-Perluorooctanesulfonamide (MPFOSA ($^{13}C_8$))	Ion [$^{13}C_8$]-Perfluorooctanesulfonate (M8PFOS ($^{13}C_8$))

Figure 2: fish species analyzed in this study

II) Analytical Process:

(The method was developed under the frame of the CONffIDENCE project [2] and validated according to Commission Decision 2002/657/EC [3].)

2g fish

1. Added into 50mL PP tube
2. Surrogates addition

6 mL Methanol

3. Shaked into vortex 1min

340mg Activated Charcoal

4. Shaked into vortex 1min
5. 3ml into PVDF centrifuge filter
6. Centrifugation at 4000rpm for 10min
7. 1ml evaporated under N_2
8. Reconstituted in 20:80 $MeOH:H_2O$ and internal standards addition

LC-MS/MS

Liquid Chromatograph:
- LC system: Thermo Scientific Aria TLX-1 (Thermo Fisher Scientific, Franklin, MA)
- Column: Hypersil GOLD PFP (50 x 3) (Thermo Scientific)
- Column before injection: BDS Hypersil C8 (50 x 3)
- Flow rate: 0.4ml/min
- Injection volume: 20µl
- Gradient elution mode:

Water : MeOH (20mM Ammonium Acetate)

Mass Spectrometer:
- Mass Spectrometrer: Thermo Scientific TSQ Vantage (Thermo Fisher Scientific, San Jose, CA)
- Ionization mode: orthogonal electrospray (ESI) in negative mode
- SRM mode
- Analysis time: 7.5 min

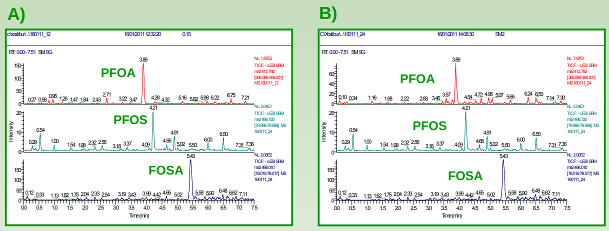

Figure 3: Extracted ion chromatograms of analyzed PFCs in: A) calibration point at 0.25 µg/l in vial and B) salmon sample from open sea (sample 2)

III) Results

		Concentration (%RSD); µg/kg		
		PFOA	PFOS	FOSA
Salmon Farm	1	< MLOQ	< MLOD	< MLOQ
	2	< MLOQ	< MLOQ	< MLOQ
	3	< MLOQ	< MLOQ	< MLOQ
	4	< MLOQ	< MLOQ	< MLOQ
	5	< MLOQ	< MLOQ	< MLOQ
	6	< MLOD	< MLOQ	< MLOQ
	7	< MLOQ	< MLOQ	< MLOQ
	8	< MLOQ	< MLOQ	< MLOQ
	9	< MLOD	< MLOQ	< MLOQ
Salmon Open Sea	1	0.61 (20)	0.19 (19)	18.18 (26)
	2	0.29 (13)	0.02 (30)	3.37 (5)
	3	< MLOQ	< MLOQ	1.16 (11)
	4	< MLOQ	< MLOQ	0.76 (16)
	5	< MLOQ	< MLOQ	1.97 (20)
	6	< MLOQ	< MLOQ	1.26 (7)
	7	< MLOQ	< MLOQ	0.52 (19)
	8	< MLOQ	< MLOQ	0.18 (15)
	9	< MLOQ	< MLOQ	0.36 (19)

		Concentration (%RSD); µg/kg		
		PFOA	PFOS	FOSA
Gilthead bream Farm	1	< MLOQ	< MLOQ	< MLOQ
	2	< MLOQ	< MLOQ	< MLOQ
	3	< MLOD	< MLOQ	< MLOQ
	4	< MLOQ	< MLOQ	< MLOQ
	5	< MLOD	< MLOQ	< MLOQ
	6	< MLOQ	< MLOQ	< MLOQ
	7	< MLOQ	< MLOQ	< MLOD
	8	< MLOQ	< MLOQ	< MLOD
	9	< MLOQ	< MLOD	< MLOQ
Gilthead bream Open Sea	1	< MLOQ	< MLOQ	< MLOQ
	2	< MLOQ	< MLOD	< MLOQ
	3	< MLOD	< MLOD	< MLOQ
	4	0.10 (8)	0.02 (26)	1.88 (12)
	5	0.08 (10)	< MLOQ	1.58 (10)
	6	< MLOQ	< MLOQ	0.14 (22)
	7	< MLOQ	< MLOQ	< MLOQ
	8	< MLOQ	< MLOD	0.13 (14)
	9	< MLOD	< MLOQ	< MLOQ

		Concentration (%RSD); µg/kg		
		PFOA	PFOS	FOSA
Turbot Farm	1	< MLOQ	< MLOD	< MLOQ
	2	< MLOQ	< MLOD	< MLOD
	3	< MLOQ	< MLOQ	< MLOQ
	4	< MLOQ	< MLOD	< MLOQ
	5	< MLOQ	< MLOQ	< MLOQ
	6	< MLOD	< MLOQ	< MLOQ
	7	< MLOD	< MLOD	< MLOD
	8	< MLOQ	0.02 (6)	< MLOD
	9	< MLOD	< MLOQ	< MLOD
Turbot Open Sea	1	< MLOQ	< MLOQ	< MLOQ
	2	< MLOQ	< MLOQ	< MLOQ
	3	< MLOD	< MLOQ	< MLOQ
	4	< MLOD	< MLOQ	< MLOQ
	5	< MLOD	< MLOQ	< MLOD
	6	< MLOQ	< MLOQ	< MLOQ
	7	< MLOQ	< MLOD	< MLOQ
	8	< MLOQ	< MLOQ	< MLOQ
	9	0.04 (19)	< MLOQ	< MLOQ

MLOD: method limit of detection established at 0.012 µg/kg (PFOA), 0.005 µg/kg (PFOS), 0.032 µg/kg (FOSA).
MLOQ: method limit of quantification established at 0.039 µg/kg (PFOA), 0.017 µg/kg (PFOS), 0.106 µg/kg (FOSA).

IV) Conclusions

The analysis of the selected PFCs concluded that this compounds were present in all analyzed samples but in most of the cases below MLOQ.

The 100% of salmon samples from open sea were detected as positives regarding the highest levels. The most contaminated sample presented levels of 0.61 µg/kg for PFOA, 0.19 µg/kg for PFOS and 18.18 µg/kg for FOSA. The 44% of the gilthead bream open sea samples were detected as a positives where FOSA presented the highest levels. In contrast, only two turbot samples (one from open sea and another one from farm) presented PFCs at quantifiable levels. Salmon and gilthead bream farm samples presented values <MLOQ, or even <MLOD, in most of the cases.

The differences of levels between same species of fish but with different origins could be explained due the presence of these PFCs in the environment. Once introduced in the environment, PFCs are transported, due to their physicochemical properties, to remote areas such as the Arctic and Antarctic oceans. Because of this, wild fishes might present PFCs levels even higher than farm fishes.

V) References

[1] Llorca, M.; Farré, M.; Picó Y.; Barceló, D.; J. Chrom. A 2009, 1216, 43, 7195-7204.
[2] Hrádková, P.; Poustka, J.; Hlousková, V.; Pulkrabová, J.; Tomaniová, M.; Hajslová, J.; Czech J.Food.Sci. (28), 2010, 4: 333-342.
[3] Commission Decision 2002/657/EC, Aug 12, 2002, implementing Council Directive 96/23/EC. Official Journal of the European Communities 2002, L221, 8-36.

VI) Acknowledgments

Thermo Scientific is acknowledged for the gift of the columns.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (*FP7/2007-2013*) under *grant agreement* n° 211326: CON*ff*IDENCE project (www.conffidence.eu).