



Screening of perfluorinated compounds in water, sediment and biota of the Llobregat River basin (NE Spain)

Julian Campo (1), Francisca Perez (2), Yolanda Pico (1), Marinella Farre (2), Damia Barcelo (2), and Vicente Andreu (3)

(1) Food and Environmental Research Group, Faculty of Pharmacy, Burjassot, Spain (julian.campo@uv.es), (2) IDAEA-CSIC, Department of Environmental Chemistry, Jordi Girona 18-26, Barcelona, Spain, (3) Centro de Investigaciones sobre Desertificación – CIDE (CSIC, Universitat de València, Generalitat Valenciana). CarreteraMoncada-Náquera km 4.5, 46113 Moncada, Valencia, Spain

PFCs present significant thermal and chemical stability being persistent in the environment, where they can bio-accumulate and adversely affect humans and wildlife (Llorca et al., 2012). Human exposure to PFCs is of concern since PFCs tend to be associated with fatty acid binding proteins in the liver or albumin proteins in blood, and have been detected in human serum, urine, saliva, seminal plasma and breast milk (Sundstrom et al., 2011). This study is aimed at the screening of 21 perfluorinated compounds (PFCs) in environmental samples by high-performance liquid chromatography tandem mass spectrometry (LC-MS/MS). The main objective is to identify target compounds at low levels in water, sediments and biota of the Llobregat River (2010), second longest river in Catalonia and one of Barcelona's major drinking water resources. PFCs were extracted from water samples by Solid Phase Extraction (SPE); from sediment by ultrasonication with acidified methanol followed by an off-line SPE procedure (Picó et al., 2012), and from biota (fish) with alkaline digestion, clean-up by TurboFlow™ on line technology coupled to LC-MS/MS (Llorca et al., 2012).

The limits of detection (LODs) and limits of quantification (LOQs) of the method were calculated by analysis of spiked river water, sediment, and biota with minimum concentrations of each individual compound at a signal-to-noise ratio of 3 and 10, respectively. The LODs and LOQs of the method in river water ranged between 0.004 and 0.8 ng L⁻¹ and between 0.01 and 2 ng L⁻¹, respectively. In sediment LODs were 0.013-2.667 ng g⁻¹ dry weight (dw) and LOQs were 0.04-8 ng g⁻¹ dw, meanwhile in biota these were 0.006-0.7 pg μL⁻¹ and 0.02-2.26 pg μL⁻¹, respectively. Recoveries ranged between 65% and 102% for all target compounds. The method was applied to study the spatial distribution of these compounds in the Llobregat River basin. For this, a total of 40 samples were analysed (14 water, 14 sediments, 12 fishes). Of the 21 target compounds, 13 were identified in water samples (PFBA, PFDA, PFHpA, PFHxA, PFHxDA, PFNA, PFOA, PFPeA, PFTDA, PFUdA, L-PFBS, L-PFHxS and L-PFOS), and their concentrations ranged between 0. 1 ng L⁻¹ (PFNA) and 2709 ng L⁻¹ (L-PFOS). Similarly, PFBA, PFDA, PFDa, PFHpA, PFNA, PFOA, PFPeA, PFTDA, PFUdA, L-PFBS, L-PFHxS, L-PFOS and PFOSA were identified in sediments samples, with concentrations ranging from 0.147 ng g⁻¹ dw (L-PFOS) to 13 ng g⁻¹ dw (PFBA). In biota similar PFC were detected, with values between 0.03 and 1738.06 ng g⁻¹. According to this study, PFCs were detected in different compartments of the ecosystem where they are bio-accumulating and, potentially, would produce adverse effects on humans.

Acknowledgements

This work has been supported by the Spanish Ministry of Economy and Competitiveness through the projects Consolider-Ingenio 2010 CSD2009-00065 and CGL2011-29703-C02-02. We also thank the persons of IDAEA for taking the samples.

References

Llorca, M., Farre, M., Pico, Y., Muller, J., Knepper, T. P., Barcelo, D., 2012. Analysis of perfluoroalkyl substances in waters from Germany and Spain. *Sci. Total Environ.* 431, 139-150.

Llorca, M., Pérez, F., Farre, M., Agramunt, S., Kogevinas, M., Barceló, D., 2012. Analysis of perfluoroalkyl substances in cord blood by turbulent flow chromatography coupled to tandem mass spectrometry. *Sci. Total Environ.* 433, 151-160.

Pico, Y., Blasco, C., Farre, M., Barcelo, D., 2012. Occurrence of perfluorinated compounds in water and sediment of L'Albufera Natural Park (Valencia, Spain). *Environ.Sci.Pollut.Res.* 19, 946-957.

Sundstrom, M., Ehresman, D. J., Bignert, A., Butenhoff, J. L., Olsen, G. W., Chang, S. C., Bergman, A., 2011. A temporal trend study (1972-2008) of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in pooled human milk samples from Stockholm, Sweden. *Environ. Inter.* 37, 178-183.