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Preliminary characterization of a candidate reference material for poly-and perfluoroalkyl substances

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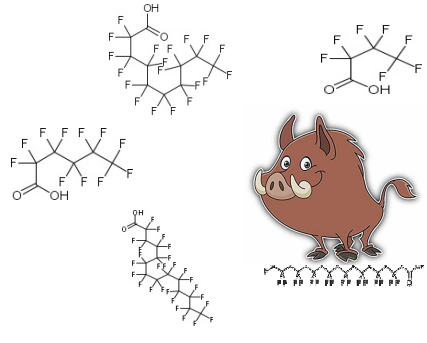
Introduction

Numerous poly- and perfluoroalkyl substances (PFAS) have been manufactured and distributed on the world market. Research on PFASs has highlighted their global distribution and impact on ecosystems and human health since these compounds are present in remote environments contaminating both humans and wildlife. Since wild species accumulate environmental contaminants, they can be used as bio-indicators of pollution. In particular, PFAS bioaccumulation has been observed mainly in blood and liver of herbivores and carnivores wild animals. As reported by other research groups, wild boar (Sus scrofa) is a good indicator for environmental pollution of PFAS contamination because it is an omnivore ingesting both flora and fauna. Furthermore, it is exposed to contaminants by water and soil. The advantage of the use of wild boar species as bio-indicator is particularly supported by the latter item its exposure to soil due to digging during foraging because soil is an important sink for PFAS [1-2]. In this context, the production of reference materials (RMs) is fundamental for the quality control and improvement of the worldwide analytical activities. The aim of this study was the preliminary characterization of a candidate RM (wild boar liver) to be used for analysis of PFASs in biological samples.

Experimental

Liver samples of 28 wild boars were collected at slaughterhouse by Veterinary Services of the Italian National Health System. Liver samples were grinded and pooled together with ultra-turrax, poured in 40 mL glass jars and sterilized. Homogeneity study was carried out analyzing 12 jars in duplicate for a total of 24 determinations. The data evaluation was performed following the harmonized IUPAC Protocol for the proficiency testing of analytical chemistry laboratories [3]. The sample extraction and purification were performed according to Kärrman et al. [4] with slight modifications. Thirty-three PFASs were analysed by an LC-Q-Orbitrap system (LC-Q-Exactive, Thermoscientific, San Jose, CA, USA). The quantification was carried out by means of isotopic dilution methodology, introducing 21 labelled internal standards.



Results and Discussion

In Figure 1, the LC-Q-Orbitrap chromatograms of some of the detected PFASs (jar 8) are shown together with a standard solution (10 ng/mL). Our results evidenced the presence of 18 PFASs (>LOQ) out of the 33 tested (table 1). The concentrations were in the range 0.18-107 µg/kg. PFOS (Perfluoro-1-octanesulfonate) was the most abundant compound (107 µg/kg), followed by PFOA (Perfluoro-n-octanoic acid) at 76 µg/kg (mean value). The other sixteen analytes were between 0.18 µg/kg and 13 µg/kg. Evaluating the 24 results from the homogeneity study, there was not evidence for outliers (Cochran's test) and, therefore, the complete data set was evaluated. The between-sample standard deviation (s_{sam}) of each PFAS was compared with the critical value (c) for the test. Being $(s_{sam})^2$ always lower than c, the produced material was considered sufficiently homogeneous.

Name	Mean	SD
PFBA (Perfluoro-n-butanoic acid)	0.41	0.08
PFBS (Perfluoro-1-butanesulfonate)	0.47	0.03
PFHxA (Perfluoro-n-hexanoic acid)	0.29	0.03
PFPeS (Sodium perfluoro-1-pentanesulfonate)	0.20	0.02
PFHpA (Pefluoro-n-heptanoic acid)	3.06	0.24
PFHxS (Perfluoro-1-hexanesulfonate)	0.67	0.10
PFHpS (Sodium perfluoro-1-heptanesulfonate)	0.39	0.05
6:2FTS (Sodium 1H,1H,2H,2H-perfluorooctane sulfonate)	0.22	0.07
PFOA (Perfluoro-n-octanoic acid)	75.76	5.76
PFOS (Perfluoro-1-octanesulfonate)	107.0	7.5
PFNA (Perfluoro-n-nonanoic acid)	11.94	0.90
8:2FTS (Sodium 1H,1H,2H,2H-perfluorodecane sulfonate)	0.18	0.05
PFDA (Perfluoro-n-decanoic acid)	7.75	0.68
PFUdA (Perfluoro-n-undecanoic acid)	6.07	0.68
PFDoA (Perfluoro-n-dodecanoic acid)	4.52	0.45
PFTrDA (Perfluoro-n-tridecanoic acid)	12.67	1.19
PFTeDA (Pefluoro-n-tetradecanoic acid)	4.46	0.54
PFHxDA (Perfluoro-n-hexadecanoic acid)	0.45	0.05

Table 1- results obtained analyzing 12 jars in twice (n=24)

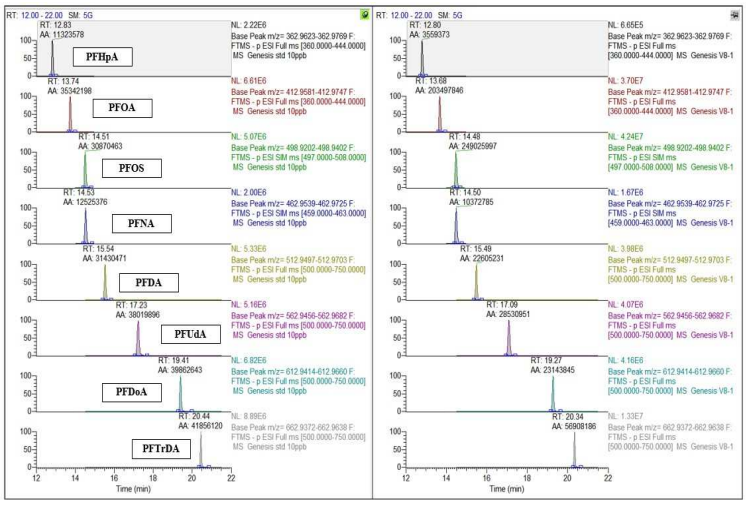


Figure 1– LC-Q-Orbitrap chromatograms of: PFASs standard solution at the concentration 10 ng/mL (left side); wild boar liver sample from jar 8 (right side)

Conclusions

The analysis of pooled wild boar liver samples further support the hypothesis that this species is a suitable bioindicator for environmental pollution of PFASs. Statistical evaluation of the concentrations of the 18 analytes found in the candidate reference material did not demonstrated their inhomogeneous distribution. Stability studies are in progress. Since, currently, PFAS contamination is representing a global issue, it is more and more important to assure reliable measurements around the world. Our study could give a small contribution to produce suitable materials for the organization of intercalibration exercises promoting standardization among laboratories, thus supporting PFAS combined/cumulative toxicity assessment.

Acknowledgements

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