Analytical improvements shown over four interlaboratory studies of perfluoroalkyl substances in environmental and food samples

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An increasing number of reports confirm the world-wide presence of the perfluoroalkyl substances (PFASs). As a consequence, the demand for qualitative and quantitative environmental occurrence data requires accurate risk assessments. To improve the analytical quality of the determination of PFASs in food and environmental samples, a 4th international interlaboratory study (ILS) was conducted in 2011. A total of 31 partners participated, and, depending on the sample matrix, up to 29 data sets were submitted. The ILS focused on food samples, as it was organized by the PERFOOD consortium in collaboration with QUASIMEME. The results showed that the cumulative experience of the participants has improved their analytical quality over four international ILSs. Several sources of errors were identified and methods to avoid them are suggested.

Keywords: Analytical quality; Environmental sample; Food sample; Interlaboratory study (ILS); Perfluoroalkyl substance (PFAS); PERFOOD consortium; QUASIMEME; Water sample

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1. Introduction

The analysis of perfluoroalkyl substances (PFASs) in environmental samples has proved challenging, and the quality of data obtained has been a major issue of concern [1]. Issues include the lack of high-quality standards (e.g., mass labeled, linear or branched), background contamination and chromatographic interferences, and poor recovery. At the same time, the analytical demands regarding limits of detection (LODs) and accurate quantification have increased since the PFASs have been shown to be omnipresent in our surrounding environment [2], and the toxicological information points towards a more complex picture of a compound group that exhibits developmental neurotoxicity [3], endocrine disruption [4,5] and reproduction disturbances [6]. These obstacles have been extensively investigated in order to satisfy the increasing demands for quantitative estimates of environmental occurrence for risk assessments, among others, via a series of international interlaboratory studies (ILSs) and workshops addressing the analytical aspects [7–10].

Several laboratories have developed methods for analysis of PFASs in food and environmental matrices to study the distribution of these chemicals in the environment and to assess the human and environmental exposure. Food intake is the major source of PFAS exposure to humans due to the amount consumed [11,12]. The European Food Safety Authority (EFSA) set a tolerable daily intake (TDI) of 150 ng PFOS/kg and 1500 ng PFOA /kg in 2008 [13]. In 2012, EFSA performed a dietary intake estimation based on 54,195 analytical results obtained for 7560 food samples reported by European member states [14]. EFSA concluded that the low proportion of quantified results (<LOQ) prevented calculation of a more realistic dietary exposure.

As the concentrations in individual food items are often reported as below the limit

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of quantification (LOQ), this can cause underestimation of the dietary exposure scenario. It was only in the late 1990s, after liquid chromatography coupled to mass spectrometry (LC-MS) became commonly available, that it was possible to determine PFAS levels in the low-ng/mL range, allowing for the first time the accurate evaluation of background levels of PFASs in biological and environmental matrices. The major PFASs are regularly monitored in food, and low LOQs are needed to determine their concentrations [15]. Typical PFAS levels in fish are at the ng/g wet weight (ww) level, the major determinand being perfluorooctyl sulfonate (PFOS) [16], whereas other food items are in the pg/g ww range [17]. Many laboratories have LOQs just around this level, so that improvements are often needed to be able to report meaningful observations. Such low levels are considered to be ''safe'' in comparison to existing toxicological evaluations, but still little is known about the combination effects between the cocktail of compounds present (e.g., in food and what is emigrating from food packaging). Hence, it is important to analyze the full spectra of contaminants. It is therefore important to improve the LODs and analytical quality of reported data. Inviting laboratories to perform interlaboratory comparisons is one important tool to identify problems and to stimulate improvements within the analytical field.

A 1st ILS, conducted in 2004/2005 showed unsatisfactory results for the determination of PFAS concentrations in human and environmental matrices [7]. The human matrices gained less unsatisfactory z-scores than the environmental matrices. The environmental samples (i.e. water, fish-liver extract and fish tissue) were analyzed by 27 laboratories and satisfactory z-scores ($|z| < 2$) were obtained by, respectively, 31%, 55% and 17% of the participants for PFOS and 22%, 40% and 25% for PFOA. The assigned values for PFOS were 37 ng/g ww in fish tissue and 20 ng/L in water. Assigned values for perfluorooctyl sulfonic acid (PFOA) were 10 ng/g ww in fish tissue and 19 ng/L in water. The relative standard deviations (RSD) between laboratories were 95–201%. The result indicated the need for the laboratories to assess their analytical procedures critically in order to reduce possible sources of error.

Meanwhile, a large number of high-quality standards had become commercially available, as had a wide range of mass-labeled standards. A follow-up study on water and fish demonstrated in 2008 that significant improvements were obtained if the participants employed high-quality native standards and multiple mass-labeled internal standards (ISs) provided by the coordinator [9]. In addition, since limited precision can be caused by low concentrations, the fish and water samples spiked with a set of PFASs were distributed to focus the interlaboratory evaluation on other analytical aspects (e.g., matrix effects, quantification principles and the determination of the accuracy of the laboratories). The satisfactory results, expressed as between-laboratory RSD to demonstrate precision, showed that the usage of mass-labeled standards is capable of correcting for different in-house analytical methods. Z-scores were not calculated in that study.

Environmental concentrations are often close to the LOQs of laboratories. The next challenge would therefore be to maintain the same level of performance at realistic (low) concentrations. The 3rd ILS on PFASs was thus organized in 2009 to assess if this could be achieved [8]. Again, the analytical performance of PFASs in human samples appeared to be better than that in the environmental samples studied (fish, water and sludge). Despite recommendations, many laboratories used only a limited number of mass-labeled standards. For PFOS, specifically, significant amounts of branched isomers present in the water, fish and blood samples appeared to be a significant source of variation, due to calibration procedures being based on only the linear isomer. Also, some results reported might have been based on the salt rather than on the anion. For the first time, sewage sludge was included in the study. The variance for the results in this matrix was substantial, showing that more effort was needed to improve methods for sludge [8].

Comparing the results between the 2008 ILS and 2009 ILS is difficult since the 2008 study was conducted in a very controlled situation in which the results were achieved. In addition to mass-labeled ISs being distributed, the data were also critically assessed in a meeting and outliers removed if technical reasons were found. Hence, the 2008 study represents a situation of ''best possible practice''. In general, the between-laboratory RSDs reported in 2009 were higher than those in 2008.

The 4th ILS focused on human samples and reported in 2009 [10]. Two serum samples and one standard solution were analyzed by 17 participants. The conclusion from the 4th ILS states that experienced laboratories world-wide are today capable of determining the most prevalent PFASs in human blood with accuracy and precision suited to serve the monitoring and exposure assessment of these compounds. As had already been indicated in the earlier ILS studies, it seems that human samples are less challenging to analyze, than environmental and food samples, which are not yet fully under control, possibly because many laboratories have a longer experience in analyzing blood than food.

The present ILS on PFASs, which is the 5th ILS on PFAS analysis but the 4th in food and environmental samples, was organized within the framework of the European Union (EU)'s PERFOOD project and in collaboration with QUASIMEME (EU's ''Quality Assurance of Information for Marine Environmental Monitoring in Europe'' project). The objectives were

(1) to assess the intercomparability of PFAS data produced by analytical laboratories, focusing on those analyzing food and drinking water, since these