

Results of an inter-laboratory polyfluorinated alkyl substances (PFAS) study based on real world samples

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Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a group of compounds which, based on their bioaccumulation potential, persistence and resistance to degradation in the environment, attract attention in a rapid manner. They have been used for decades in a variety of consumer products and industrial applications and can be found in trace levels in the environment. The analysis of these components are increasingly requested. However, standards span a wide range of concentrations in various countries across the globe. Also, analytical methods are in flux in terms of list of analytes, limits of quantitation and detection.

In order to understand the variability of the analytical data from laboratories in North America and Europe, The Dow Chemical Company initiated and conducted an inter-laboratory study based on real world, non-spiked samples. This concept is based on our annual proficiency test program that we developed and have implemented for several years as part of our contract laboratory quality assurance program. This program uses real world, non-spiked samples of varying concentrations from various locations to determine the quality and performance of the laboratories for key analytical parameters (PCDD/F, VOC, SVOC, metals and others) [1,2].

Materials and methods

PFAS containing water, a blend of retainers and left-overs from various samples of different origin, was provided by one of Dow Chemical's preferred contract laboratories. Upon arrival at Dow's Environmental Analytical Laboratory (EAC), the blend was mixed with different non PFAS containing waste waters in order to provide a background matrix simulating mixed plumes. The blend was then pre-diluted to obtain a more reasonable concentration range and to avoid foaming. This blend ("neat" sample A), while being continuously stirred, was transferred into 250 ml HDPE bottles in 50 ml portions. From this blend a 1:2 dilution was prepared by placing five 25 ml portions into each 250 ml bottle and then adding an additional 125 ml of water. A duplicate set of 1:2 dilution samples was created and provided to the laboratories as non-disclosed duplicate sample B and C. In addition, a sample D was submitted which consisted of laboratory tap water in which polyfluorinated polymers containing material commonly

used in laboratories was soaked for about a week (stop-cocks, coated stir-bars, boiling chips). In contrast to the other samples, this water was spiked after filtration at a level of 5 ng/l with a mix of 12 of the 15 PFAS compounds to be analyzed in this study (except PFOSA, 6:2- and 8:2-FTS).

For each sample, 3 bottles were provided to the laboratories. In addition, two extra bottles were provided for sample C along with the request for the analysis of a laboratory duplicate analysis. We asked the laboratories to use the entire content of the bottle to avoid the potential impact of sub-sampling. No specific method was required. It was requested that each laboratory include 15 different groups of PFAS compounds and that they should also indicate if the analysis included were only the linear components or also contained the branched PFAS compounds as well. In addition, a reporting limit of 2 ng/l was requested (1 ng/l for PFOS and 10 ng/l for the 6:2 and 8:2 Fluorotelomersulfonate). Finally, the type of recovery and the recovery rate of the surrogate standards used, along with information about the application of the isotope dilution method, was requested. In total, 13 laboratories in the USA, Canada and Europe were invited to participate in this inter-laboratory study. Of those, 11 agreed to participate.

Results and discussion

For the evaluation of the data, analytical results below the laboratory reporting limits were not taken into consideration as they only represent an estimate. The results for samples B and C, as well as the requested laboratory duplicate, C-Dup, were averaged for each laboratory. The data is presented in the following figures, where the numbers represent the assigned participant numbers.

Figure 1: Results for the neat sample A (the numbers refer to the participating laboratories)

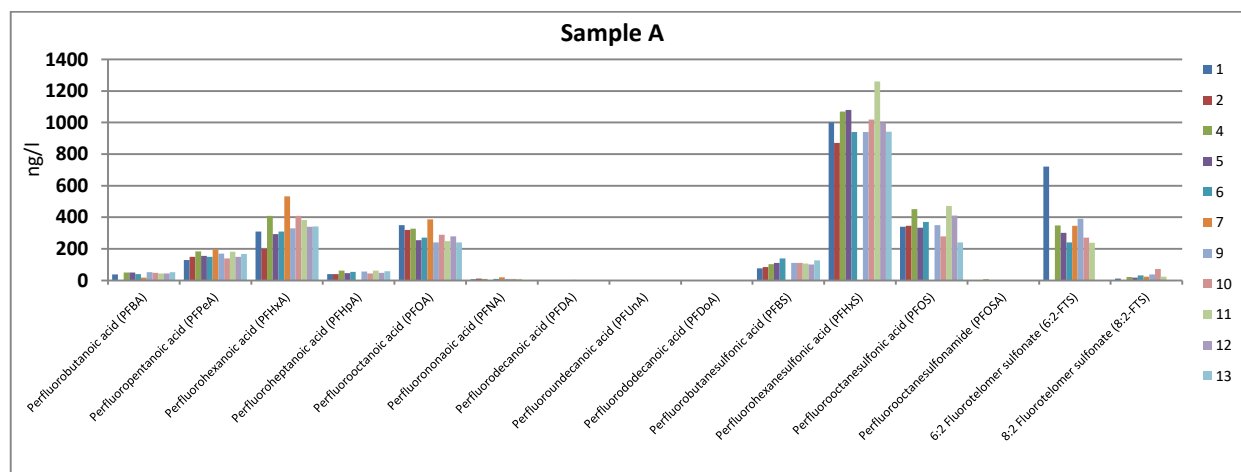
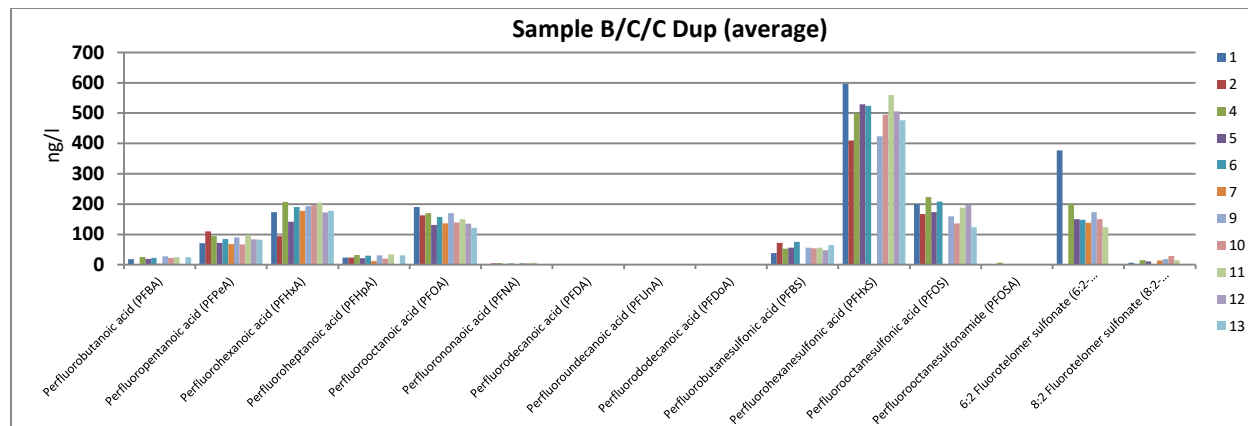
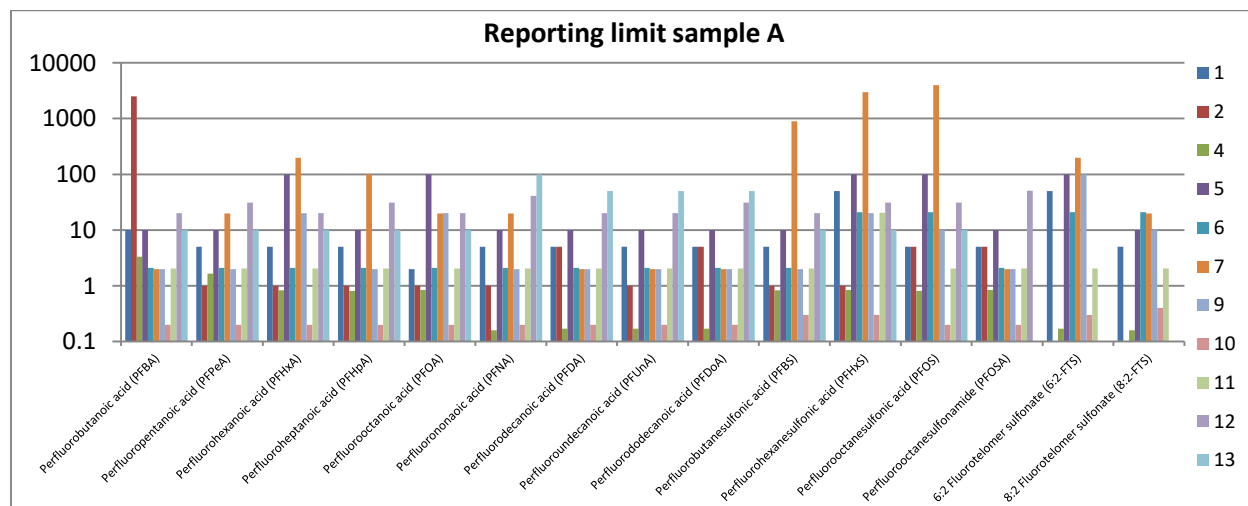


Figure 2: Results for the duplicates of the diluted samples B, C and C-Dup (the numbers refer to the participating laboratories)



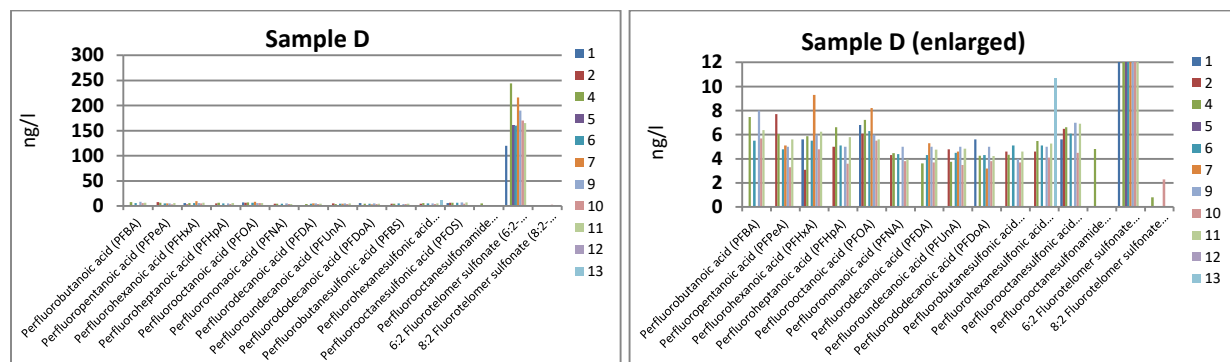
The analytical data from all laboratories for the quantified components, except for 1 lab with 6:2-FTS, show very small variability. This result is exceptional, especially when taking into account that no explicit method was required. Some participants followed the US EPA method 537 strictly or with minor modifications while others used their own procedure. It indicates also that the analytical procedures used by the North American and European laboratories deliver very similar results.

Figure 3: Reporting limits (the numbers refer to the participating laboratories)



The biggest discrepancy observed, was for the reporting limits for all target compounds which varied from 0.2 ng/l to >2,000 ng/l as depicted in figure 3 (note the logarithmic scale). With the increasing demand for lower quantitation limits due to lower thresholds, this indicates a need for establishing reliable analytical procedures in the lower concentration ranges. The results of sample D (figure 4), laboratory water in which laboratory articles with fluor-containing polymers were soaked for a week, demonstrate the need for an absolutely PFAS free environment in the laboratory. The apparent inert laboratory material is capable of releasing PFAS components in significant amounts.

Figure 4: Results for sample D (the numbers refer to the participating laboratories)



6:2-FTS were found at a level of 130 – 245 ng/l. which is the largest variability for a component group in the whole study. Also the recovery rates for the 6:2-FTS (110-260%) varied a lot across the laboratories compared to most of the other components in this study. This could indicate some analytical challenges for this group of components. The laboratories which were able to quantify down to the requested reporting limit were also able to recover the spiked components (5 ng/l) very well. The slightly higher levels for the tetra- to octafluorinated alkyl acids and PFOS may indicate a slight contamination from the soaked material.

Acknowledgements

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References

1. Wilken M., Abel T. (2010) Organohalogen Compounds Vol. 72, 812-815
2. Richardson J, Wilken M (2014), Poster presented at NEMC conference in Washington DC, 2014