Emerging Pollutants of Environmental Concern: A new Proficiency Testing (PT) Scheme for Per and polyfluorinated alkyl substances (PFAS) in groundwater

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INTRODUCTION

The attention of analytical companies and legislators is moving from the 'traditional' pollutants to a new group of "emerging" environmental contaminants. These contaminants are increasingly of concern due to their widespread occurrence, their potential toxicity to mammals or other biota and their ability to persist in the environment, often resulting in bioaccumulation. Per and polyfluorinated alkyl substances (PFAS) are a group of over 4,500 widely used, synthetic chemicals, that accumulate over time in the environment and in the human body. The most widely used, and most well-known PFAS, are perfluorooctanoic acid (Figure 1, PFOA) and perfluorooctane sulfonic acid (PFOS).

The analysis of PFAS presents some considerable challenges for various reasons, one being the actual number of substances defined under PFAS, as well as the physicochemical properties and concentration of the substances in environmental samples. Accurate and robust analytical methods are essential for the detection and quantification of PFAS in water and will assist in the understanding on the prevalence and transportability of these compounds between different environments e.g., between soil and groundwater. The US Environmental Protection Agency (EPA) has developed, validated, and published three analytical methods for the analysis of PFAS in potable (treated) water, all based on LC-MS/MS. The methods generated acceptable method performance data for groundwater containing up to 300 mg/L of total dissolved solids (TDS)/hardness.

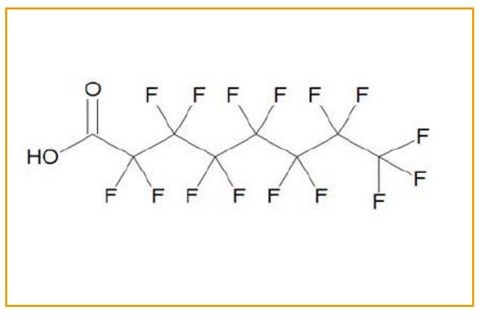

Figure 1: Perfluorooctanoic Acid (PFOA)

SAMPLE FORMAT

AQUACHECK PT scheme has been in continuous operation since 1985. Participation in the scheme allows laboratories to identify problems before they affect the quality and safety of waters. High quality analysis of PFAS contaminants depends on laboratories having access to reliable and robust testing methodologies and reliable and good quality PT.

The sample is provided as 2 x 1L LDPE bottle containing ground water and 1 x 1mL amber ampoule with spiking solution, produced by Dr Ehrenstorfer Gmbh. Participants were provided with comprehensive instructions on how to perform the PT exercise (Figure 2).

In the current round, 17 PFAS were added in the spiking solution, all of which are included in the revised Water Framework Directive published by the European Commission which contains legislative limits for 20 PFAS. There is a potential to provide all the 47 PFAS listen in the appendix of the AQUACHECK Scheme description which is based on the requirements of the Drinking Water Inspectorate (DWI) in England and Wales

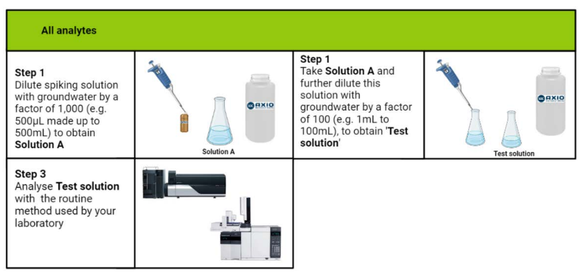

Figure 2: Instructions provided to participants

PARTICIPANTS

The first round was distributed to participants in June 2023.

The majority of the participants were from the United Kingdom, making up approximately half of all laboratories which took part. The other half of the participant labs were located in 11 different countries, predominantly in Europe. (Figure 3).

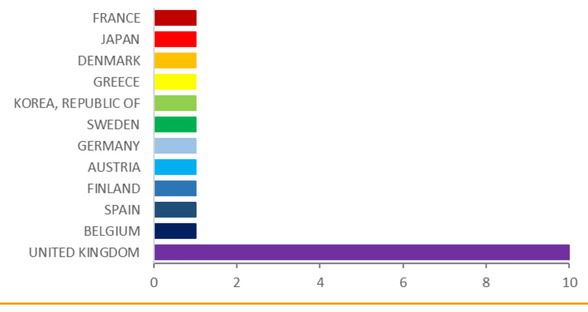

Figure 3: Participant Country of Origin

RESULTS AND DISCUSSION

The 17 PFAS components were present in the prepared test material at concentrations of 52 to 130 ng/l. The performance of the participants in the first round of this PFAS sample was generally good. The robust standard deviation of the returned results was 11 – 19%, relative to the assigned value, for 12 of the components, three were 22 – 27%, whilst for PFDS and PFTrDA the robust standard deviation was 32 and 33% respectively (Table 1).

Using the median of the participant results as the assigned value and the robust standard deviation (MADe) as σPT the rate of satisfactory performance amongst the participants was good, ranging from 74 to 96% depending on the analyte in question. The histogram of the z-score range is shown as an example for PFDS (Figure 4).

Only a limited number of the participants reported the method used for analysis. Those labs who did report their method of analysis used the EPA 1633 or EPA Method 537 & 537.1: LC-MS/MS methods.

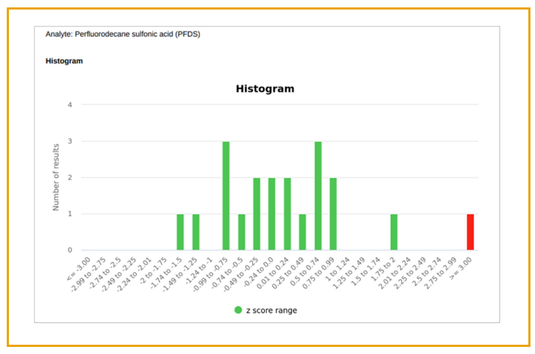

Figure 4: Histogram of the performance scores (z score) obtained for PFDS

Compound	Abbreviation	AV (ng/l)	σPT (ng/l)	n	Satisfactory %
Perfluorobutanoic acid	PFBA	74.7	10.01	21	85.7
Perfluoropentanoic acid	PFPA	99.9	11.49	21	85.7
Perfluorohexanoic acid	PFHXA	126.8	15.35	21	90.5
Perfluoroheptanoic acid	PFHBA	55.2	8.9	22	95.5
Perfluorooctanoic acid	PFOA	129.1	22.17	21	76.2
Perfluorononanoic acid	PFNA	125.9	23.43	21	81
Perfluorodecanoic acid	PFDA	92.6	24.91	21	90.5
Perfluoroundecanoic acid	PFUNDA	52.3	12.61	21	90.5
Perfluorododecanoic acid	PFDODA	70.7	15.87	20	85
Perfluorotridecanoic acid	PFTRDA	93.1	30.85	19	78.9
Perfluorobutane sulfonic acid	PFBS	72.8	9.34	21	95.2
Perfluoropentane sulfonic acid	PFPS	117.3	18.09	22	95.5
Perfluorohexane sulfonic acid	PFHXS	78.4	10.97	21	85.7
Perfluoroheptane sulfonic acid	PFHPS	127.9	18.54	20	80
Perfluorooctane sulfonic acid	PFOS	88.9	15.79	21	85.7
Perfluorodecane sulfonic acid	PFDS	95	30.4	20	95
Perfluorononane sulfonic acid	PFNS	68.8	12.68	19	73.7

Table 1: Statistical parameters obtained from the reported participant results

CHALLENGES - PFAS ISOMERS

During the last few years, the difference between isomeric forms of PFAS substances has emerged as an additional factor which affects the physicochemical properties of the compounds. This can have an effect in the adsorption on solid phases, the distribution in different environmental compartments etc. Some researchers suggest that linear PFAS are more readily adsorbed to soil and sediments, where as branched isomers are more likely to remain in water compartments probably due to the differences in polarity between the two isomers.

NEXT STEPS

LGC AXIO provides solutions to support the quality control activities of laboratories undertaking work in this field. Through our range Dr Ehrenstorfer reference materials labs can use fully characterised, including isotopic composition, reference standards during method development, for spike recovery and as routine analytical calibration standards.

Dr Ehrenstorfer are working on offering all 20 PFAS included in the EU Water Framework Directive.

The abundance of PFAS in the environment may sometime lead to accumulation in fish, seafood, meat, and other food products, therefore, LGC AXIO has added a new PT sample in the QMAS PT scheme, for the determination of PFOS, PFOA, PFNA, PFHxS and the sum of the four PFAS in fish e.g., carp or seafood as per the Commission Regulation (EU) 2388/2022.