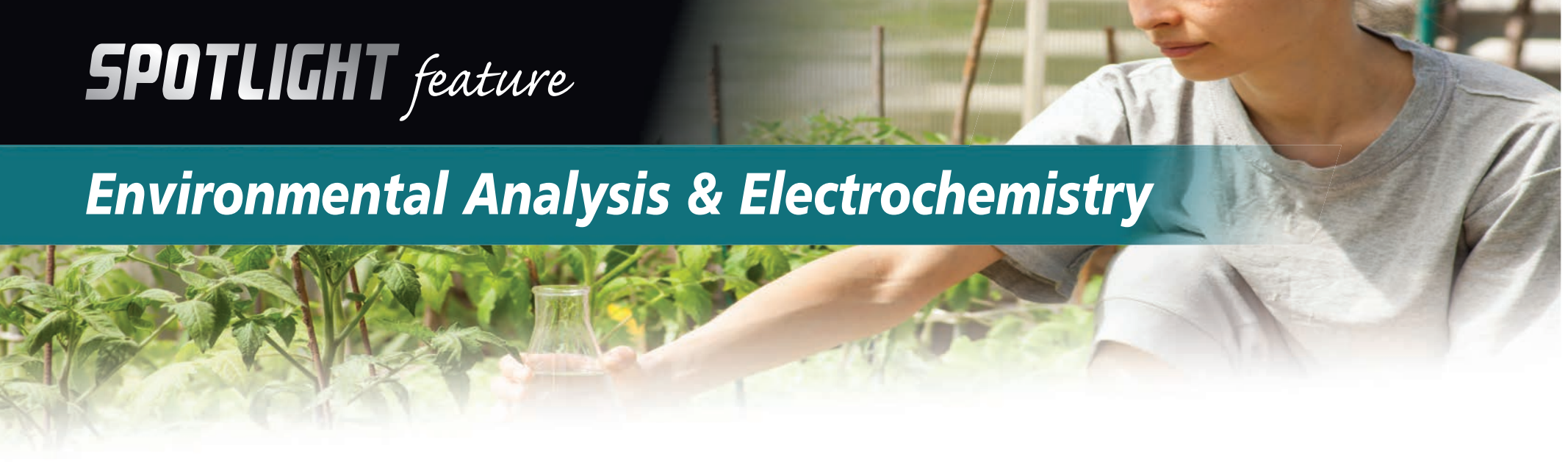
SPOTLIGHT feature

Environmental Analysis & Electrochemistry



Overview of perfluorinated compounds residues in water analysis through proficiency-testing scheme results

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Interest for the detection of perfluorinated compounds in water have increased in the past few years due to their harmful effect on the environment and human health [1, 2]. These molecules are also part of the list for the approval of the French Environment Ministry [3] with a diminution of their required quantification limits since 2021. Thus, the BIPEA (Bureau Interprofessionnel d'Etudes Analytiques) decided to launch in 2015 a dedicated proficiency testing scheme (PTS) for perfluorinated compounds in surface water to allow the laboratories to test and enhance their abilities for these determinations, especially in the framework of laboratories accreditation according to ISO/IEC 17025 standard [4]. Other molecules were added in 2016, which led to an increase in the number of participants with better robustness of the statistical tests. Since 2018, twice a year, a proficiency test with two series of samples spiked with 7 molecules is organised: perfluorodecanoïque acid (PFDA), perfluorodecane sulfonic acid (PFDS), perfluoroheptanoïc acid (PFHpA), perfluorohexane sulfonic acid (PFHxS), perfluorohexanoïc acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS). Eleven rounds were performed so far, which allows now to draw an overview of the results and performance met in this PTS, especially regarding the number of results obtained for the different molecules, the related dispersion and some information about the recovery rate.

Materials and Methods. Sample production and shipment

The most crucial aspect for the implementation of a proficiency-test program is the production of homogeneous and stable samples.

For this PTS, a batch of river surface water is homogenised in an adapted tank and distributed into one-litre brown glass bottles. Each bottle is then spiked individually with a solution containing all the molecules.

The homogeneity is checked through the analysis of a few molecules by an external accredited laboratory. Ten samples from the manufactured series are analysed in duplicate to determine the between-samples standard deviation *(see Table 1).*

Table 1. Example of homogeneity control for PFHxA (unit: µg.l^{-1}; between-samples SD: Ss= 0,001).

Sample number	Portion 1	Portion 2	Mean
1	0,027	0,030	0,029
2	0,029	0,032	0,031
3	0,030	0,028	0,029
4	0,030	0,038	0,034
5	0,039	0,040	0,040
6	0,022	0,042	0,032
7	0,023	0,038	0,031
8	0,014	0,027	0,021
9	0,031	0,035	0,033
10	0,030	0,024	0,027

For each series, a one-litre bottle is provided to the participants in order to provide to them enough volume to conduct their analytical process.

The parcel with the bottles is then shipped to all participants by express carrier under refrigerated conditions, using cooling gels, with a target temperature at (4±3) °C.

Analyses by laboratories

Laboratories are invited to analyse these samples using the technique or method they want, like the LC/MS or LC/MSMS and submit their analysis results via electronic reply forms, in which they can also provide additional information about their method and the date of analysis for example.

Statistical treatments

The statistical treatments of the quantitative returned results are carried out in accordance with ISO 13528 standard [5]. The assigned values (x_{pt}) are estimated from the robust mean of all the results, except obviously erroneous values. The standard deviation for proficiency assessment (σ_{pt}) is set to 30% of the assigned value. The use of such a determined value, commonly used in the field and discussed in participants meeting, allows to have an assessment that is independent from the obtained results and consistent through time. This is especially useful when there is a limited number of results, which could lead to have a wide and fluctuant dispersion of the results.

The quantitative results (x) could be evaluated and classified through z-scores, where $z = \frac{(x - x_{pt})}{\sigma_{pt}}$

- for $z \leq |2|$, the result is considered to be acceptable,
- for $|2| < z < |3|$, the result is considered to be a warning signal,
- for $z \geq |3|$, the result is considered to be an action signal.

The interlaboratory comparison report is validated by both Bipea and an external technical expert, and is then circulated to the participant.

Results and Discussion

The first important data is the participation and the number of results. There is an average of 18 registered participants since 2016. This number shows the interest for this kind of analyses. It is to be noted that the participants that give results usually do it for all the molecules offered, at the notable exception of the PFDS.

Below is *Table 2* with the number of results per molecules over time.

Table 2. Participation over time for perfluorinated compounds.

	Dec-16	May-17	Dec-17	May-18	Dec-18	Apr-19	Dec-19	Apr-20	Dec-20	Apr-21	Dec-21
PFDA	6	9	8	6	11	14	14	13	14	12	15
PFDS	-	-	3	2	3	6	7	7	11	11	13
PFHpA	-	-	-	6	10	15	16	13	15	13	17
PFHxS	7	10	8	9	10	15	16	13	15	13	17
PFHxA	-	-	-	7	9	14	16	13	15	13	17
PFOA	8	11	10	9	11	16	16	12	15	14	17
PFOS	8	12	10	9	11	16	17	12	16	12	17

The dispersion of the results, provided as CV% (robust standard deviation of the results / robust mean of the results (in %)), allows to describe how strong or not is the consensus met *(see Figure 1)*.

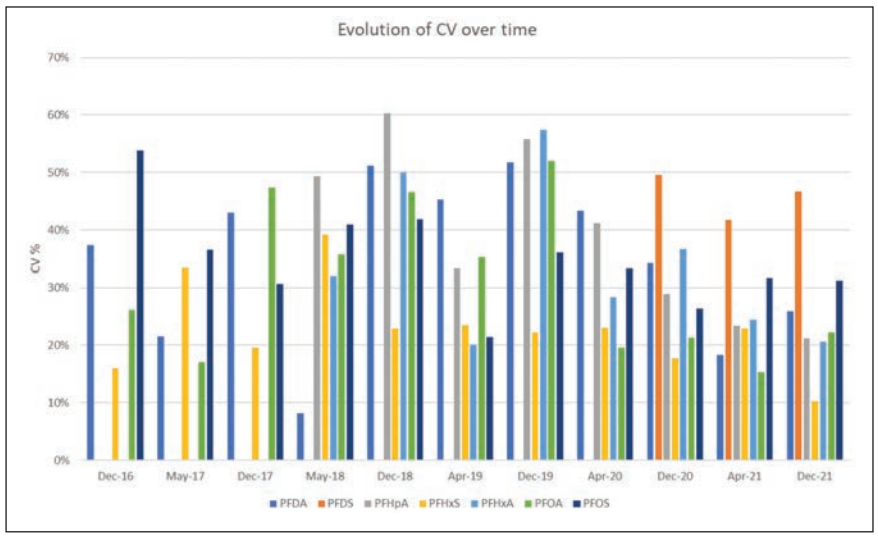

Figure 1. CV% over time.

The dispersion of most of these molecules shows the difficulty to analyse this kind of matrix. Though, several high CV can be attributed to a smaller number of participants at the time, in the case of the PFDS for instance. A slight decrease in the dispersion of PFDA, PFHpA and PFOA between December 2018 and December 2021 can be observed.

At the considered concentration (from approximately 0.040 to 0.250 µg.l $^{-1}$) and despite a limited number of data, there seems to be no correlation between the assigned value and the CV for these molecules. Below is the example of PFHxS and PFOS *(see Figure 2)*.

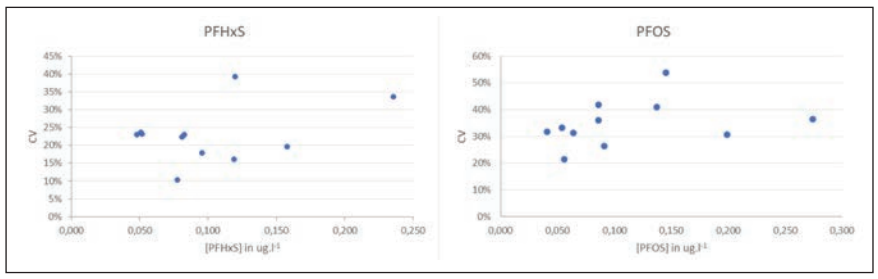

Figure 2. CV% against concentration.

Some information can also be obtained for the spiking performed on the samples. The consensus value (or assigned value) obtained in the tests can actually be compared with the theoretical spiking value *(see Figure 3 and Figure 4)*.

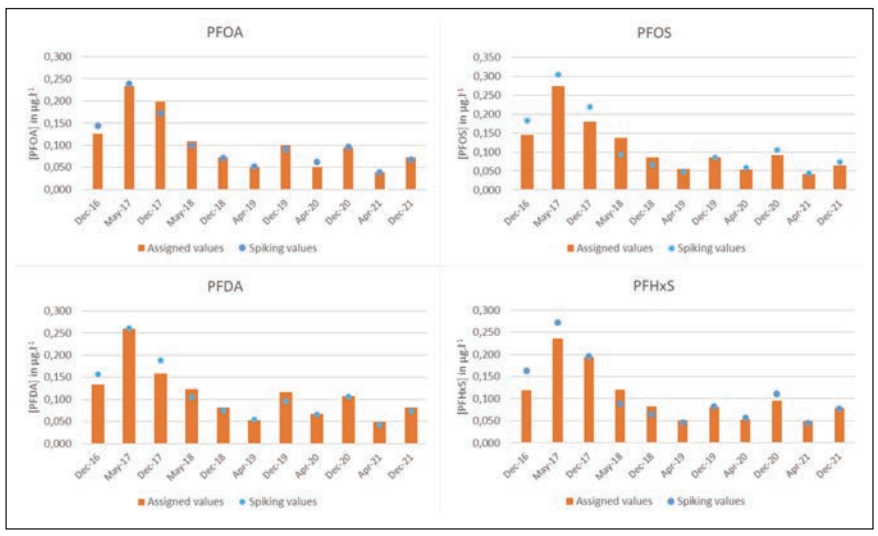

Figure 3. Spiking performance (1).

Overall, the spiking values are well recovered when the molecules are found and can be divided into 3 main categories:

- Average recovery rate (absolute) below 10%: PFHpA, PFOA and PFDA
- Average recovery rate (absolute) between 10% and 20%: PFHxS, PFOS and PFDS
- Average recovery rate (absolute) above 20%: PFHxA

For PFHxA, it seems that an occasional natural contamination of the matrix is plausible to justify the highest recovery rate. All of the molecule are added from the same solution and no systematic overestimation of this molecule is observable. Neither is a general overestimation of the molecules. In particular, for December 2020, the assigned value represents +48% of the spiking, suggesting pre-existing PFHxA in the matrix.

There seems to be no major stability or analytical issues considering that most of the molecules are found every time.

In the case of PFDS, the lack of participants played an important part in the absence of assigned values for several tests.

Overall, the performance observed on *Figure 5* is satisfactory as no mean % of untrue is above 20% despite 3 individual tests reaching 30%. Error bars represent the standard error of the mean. There was no specific evolution over the years (see *Figure 6* below for two examples), the performance has stayed quite stable over time if we exclude the very start of the PTS. Only 2 laboratories out of the 31 considered over all the campaigns have a global percentage of untrue results above 30%. These analyses seemed to be already well handled by a majority of participants from the very beginning of the PTS.

It is to be noted that a large majority of untrue results were so by overestimation (87.5%). This suggests a positive bias for these analyses.

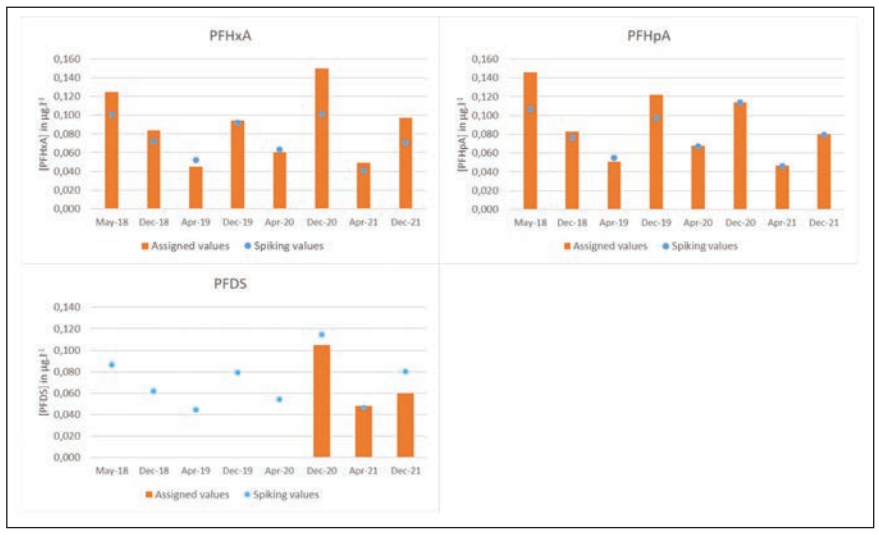

Figure 4. Spiking performance (2).

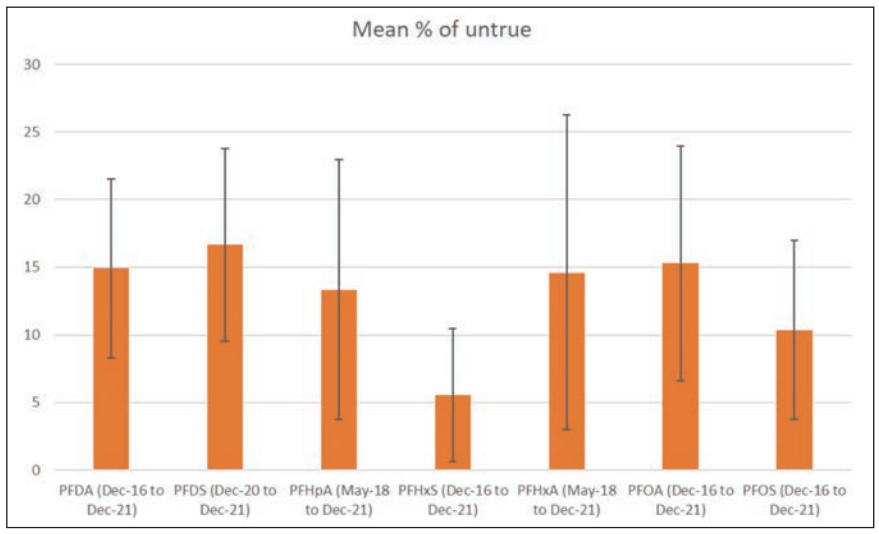

Figure 5. Mean performance of the participants (Dec-16 to Dec-21).

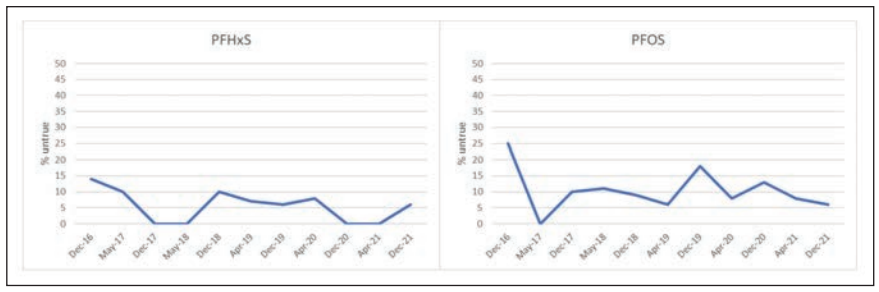

Figure 6. Performance of the participants for PFHxS and PFOS (Dec-16 to Dec-21)

Conclusion

The surveillance of perfluorinated compounds in water has been developing over the years. In order to meet this new demand, a dedicated proficiency testing scheme allows the participants to have a better control of their routine analyses and to potentially evaluate themselves on new molecules of interest. This kind of test is very useful to assess the performance of laboratories and detect bias or non-compliant results; thus, act as a warning signal for the implementation of corrective and/or curative actions in the laboratories. Participation in several proficiency tests per year is of considerable importance, particularly to detect drift or bias in the results, through the use of control charts. Proficiency tests are an essential tool for the quality management of laboratories and for the continuous improvement of their analytical performance.

The number of results is now sufficient after a few years of testing and grants the possibility to get robust data: laboratories performance, spiking recovery, stability and participation. In the case of perfluorinated compounds, the participants have shown their ability to conduct these analyses in a satisfactory manner despite a challenging matrix. There was no significant evolution over time in the performance by looking at the percentage of untrue results, though the dispersion has slightly improved for PFDA, PFHpA and PFDA.

The need for such testing might grow as the regulation tends to be stricter for these molecules in fresh water.

References

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2. Stahl, T., Mattern, D. & Brunn, H. Toxicology of perfluorinated compounds. Environ Sci Eur 23, 38 (2011).

3. Approval of the French Ministry of Environment: http://www.labeau.ecologie.gouv.fr/

4. International standard: ISO/IEC 17025:2017 - General requirements for the competence of testing and calibration laboratories.

5. International standard: ISO 13528:2015 - Statistical methods for use in proficiency testing by interlaboratory comparisons