

Application Note



Passive sampling for the analysis of **13 perfluorinated compounds (PFAS)** in river water using **AttractSPE® POCIS - PFAS**



This application note describes an in-vitro experiment over a period of 7 days for the passive sampling and analysis of 13 Perfluorinated compounds (PFAS) in river water. The method relies on **AttractSPE® POCIS – PFAS** to catch perfluorinated compounds in water prior to their analysis by LC-MSMS.

Perfluorinated compounds (PFAS or PFCs) are a large family of molecules consisting of varying lengths of fluorocarbons chains with a functional group such as carboxylic or sulfonic acids attached. They have been widely used for more than 50 years in various products, such as firefighting foams, hydrophobic and nonstick coatings, or surfactants to cite a few examples. Their nature makes them particularly chemically inert and very resistant to degradation in environment. For this reason, some PFAS are classified as persistent organic pollutants (POPs). Finally, PFAS are strongly associated with a variety of human disorders such as neurotoxicity, immune deficiency, and cancer[1].

Passive sampling allows the surveillance of contaminants in water surfaces over a short period (less than 7 days) or longer (1 month), in which no energy, maintenance or control is necessary. An average of the concentration of contaminants is then determined in laboratory.

Table 1. List of the 13 tested PFAS

Compound	Abbreviation	CAS number	Chemical composition
Perfluorobutanoic acid	PFBA	375-22-4	C ₃ F ₇ -CO ₂ H
Perfluoropentanoic acid	PFPeA	2706-90-3	C ₄ F ₉ -CO ₂ H
Perfluorohexanoic acid	PFHxA	307-24-4	C ₅ F ₁₁ -CO ₂ H
Perfluoroheptanoic acid	PFHpA	375-85-9	C ₆ F ₁₃ -CO ₂ H
Perfluorooctanoic acid	PFOA	335-67-1	C ₇ F ₁₅ -CO ₂ H
Perfluorononanoic acid	PFNA	375-95-1	C ₈ F ₁₇ -CO ₂ H
Perfluorodecanoic acid	PFDA	335-76-2	C ₉ F ₁₉ -CO ₂ H
Perfluorobutanesulfonic acid	PFBS	375-73-5	C ₄ F ₉ -SO ₃ H
Perfluorohexanesulfonic acid	PFHxS	355-46-4	C ₆ F ₁₃ -SO ₃ H
Perfluorooctanesulfonic acid	PFOS	1763-23-1	C ₈ F ₁₆ -SO ₃ H
Hexafluoropropylene oxide dimer acid	HPFO-DA	13252-13-6	C ₃ F ₇ -O-CF(CF ₃)-CO ₂ H
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	C ₆ F ₁₃ -C ₂ H ₄ -SO ₃ H
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	C ₈ F ₁₇ -SO ₂ -N(C ₂ H ₅)-CH ₂ -CO ₂ H

1 Description of the passive sampler

AttractSPE® POCIS – PFAS (Polar Organic Chemical Integrative Sampler) are passive samplers for water monitoring of a wide range of perfluorinated compounds. A sorbent under the form of powder is trapped between nylon membranes that are themselves trapped between two stainless steel disks (**Figure 1**). Several formats and chemistries are available to best suit each application. The sorbent can be spiked with several PRC to improve the accuracy of the method.

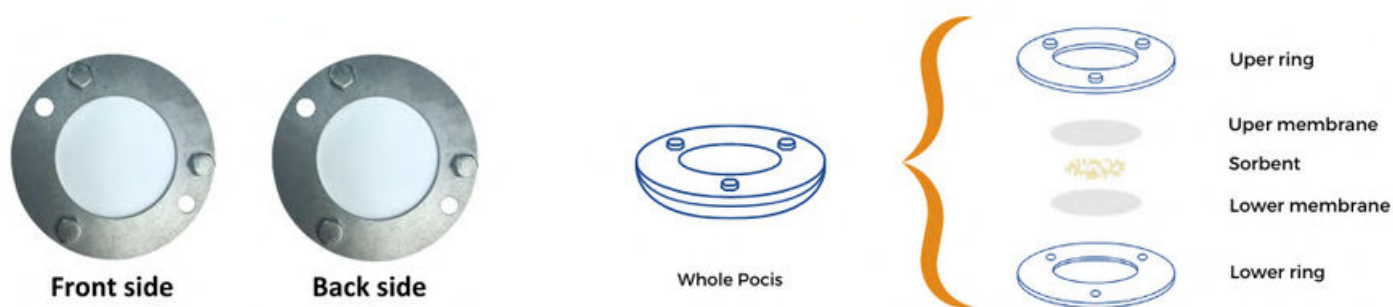


Figure 1. Description of POCIS

2 Description of the assembly

The experiment was processed in a fish tank made of glass (40x40x40cm). 50 liters of river water (Le Cailly, Le Houlme, France) spiked at $1\mu\text{g/L}$ with the 13 PFAS was at first put into the tank. For the entire duration of the experiment, water from the tank was constantly drained out and replaced with unspiked river water using a peristaltic pump at the speed of around 14 L/Day. A spiking solution of 13 PFAS was injected directly into the tank using HPLC pump at a flowrate of 0.2mL/min (288mL/day) to keep the concentration constant in the tank. The water in the tank was kept agitated using a rod with propeller attached to a drill at a speed of 120 RPM to simulate a flow. The temperature during the experiment was around 19°C and thus considered constant. The pH measured is 6.5.

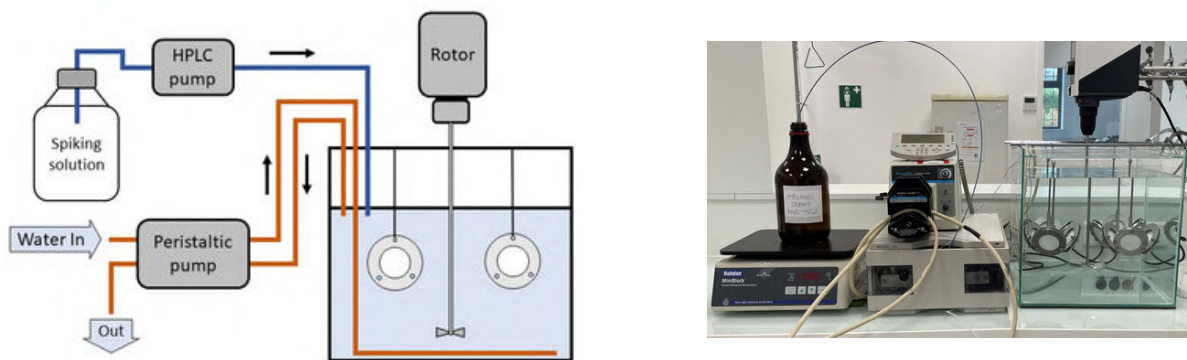


Figure 2. Assembly diagram (left) and picture of the experimental setup (right)

3 Proceeding of the experiment

The sampling capacity of the POCIS was tested from 1 to 7 days with two POCIS for each day (identified as a set), for a total of 14 passive samplers. At any moment 8 samplers were simultaneously immersed in the tank following the immersion schedule (**Figure 3**). For example, after 1 day, the “1 day set” was removed from the tank and replaced by the “6 days set”

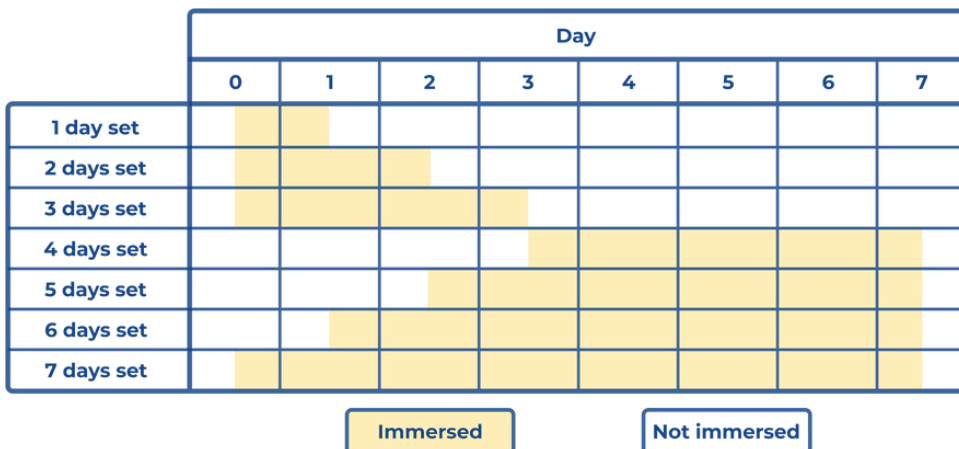


Figure 3. Immersion schedule.

After the removal of a set, the POCIS were rinsed with ultrapure water and extracted prior to analysis.

4 Extraction procedure

After the removal of each POCIS from the tank, it was rinsed with ultrapure water. An extraction procedure was realized on the sorbent, and another one on the pair of membranes.

The procedure for processing each POCIS is as follows:

Extraction of sorbent:

- 1. Sorbent recovery:** The POCIS is opened by unscrewing each bolt and the upper stainless steel disk is removed. The two nylon membranes are carefully separated, and the sorbent is collected from the surface of each membrane into an empty SPE cartridge (containing a frit) with the help of a manifold with vacuum and ultrapure water. A frit is then pushed into the cartridge to trap the sorbent. The two membranes are set aside for later extraction.
- 2. Washing/drying:** The cartridge is washed with 2 mL of ultrapure water at pH = 4 (adjusted with formic acid) then dried by applying full vacuum for 1 minute.
- 3. Elution:** The molecules are eluted from the cartridge with 2 mL methanol, followed by 4 mL 0.2% NH₄OH in methanol.
- 4. Analysis:** The eluates are then agitated and analyzed as is (or diluted with methanol if too concentrated) by LCMSMS. Each cartridge is dried, and the sorbent weighted.

Extraction of membranes:

- 1. Extraction:** Each pair of membrane, after sorbent removal, is put into a 15 mL polypropylene tube. 8 mL of methanol is added. The tube is agitated for 30 minutes.
- 2. Analysis:** The eluates are agitated and analyzed as is by LCMSMS.

After the extraction procedure, the concentration of the molecules in each passive sampler (sorbent + pair of membranes) were simultaneously analyzed by LC-MS/MS (**Table 2**).

5 Conditions of analysis

During analyses, some analytes of interest are also likely to be found in mobile phase or LC parts and tubing. These analytes concentrate at the front of the LC column during each sample run, leading to analysis interference due to contamination. To change LC parts and tubing and control solvents purity is very expensive and time consuming. Moreover, some contaminant may never be totally removed. The other solution is the use of a delay column.

A delay column is put between LC pumps and sample injection (**Figure 4**). It allows the analyte of interest coming from the LC device to concentrate at the front of the delay column instead of LC column, while the analyte coming from sample injection will concentrate directly on the LC column.

This will lead to a longer retention time for the analyte from LC device because it must pass through the delay column in addition to the LC column whereas the analyte from sample injection must only pass through LC column (**Figure 5**).

This solution is very easy to put in place and is cost effective.

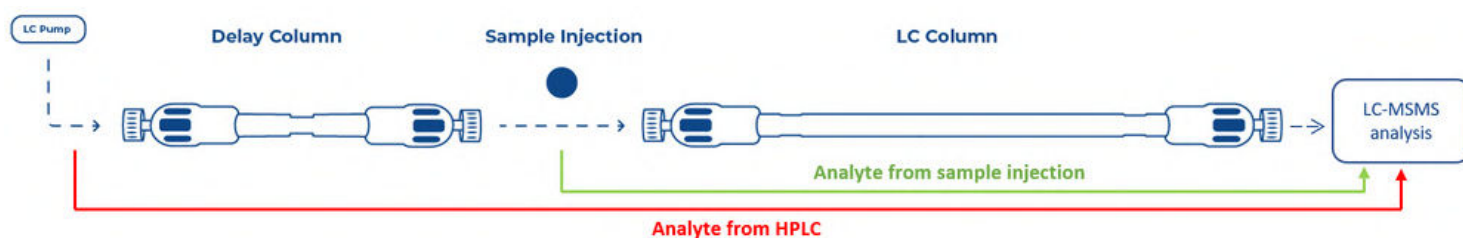


Figure 4. Installation of Delay column for LC analysis.

Figure 5. Effects of a delay column on samples. A: Blank sample without delay column. B: Spiked sample without delay column. C: Blank sample with delay column. D: Spiked sample with delay column.

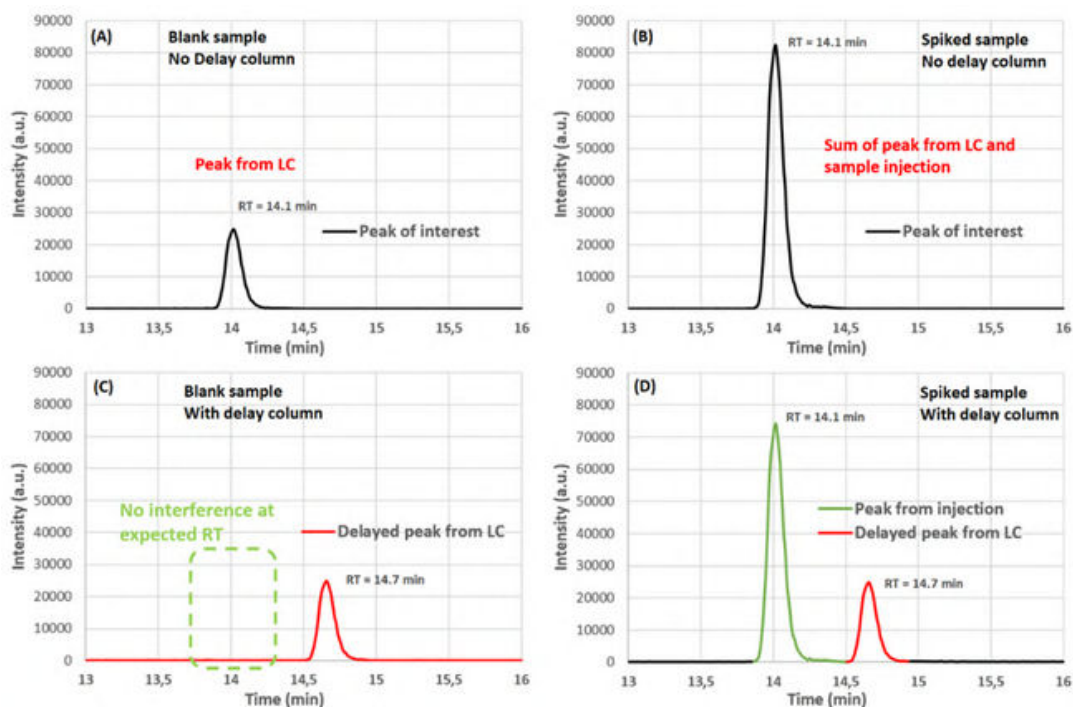


Table 2. LC-MS/MS Conditions of analysis.

LC Conditions			MS/MS Conditions				
LC Dionex U3000			Qtrap 4000 ESI- MS/MS				
Column : SilactHPLC LC-PFAS 150*2.1mm at 40°C			Curtain gas : 30				
Delay column : SilactHPLC Delay-PFAS 50*2.1mm			CAD : High				
Injection volume : 5µL			IS : -4500V				
T° sampler : 10°C			Temperature : 400°C				
Flow rate : 0.25mL/min			GS1/GS2 : 50/50				
Time (min)	10mM Ammonium Acetate (in water)	Methanol	Analyte	Retention time (min)	Q1 (m/z)	Q3 (m/z)	CE (V)
0	60%	40%	PFBA	4.0	213.0	168.8	-14
			PFPeA	7.5	263.0	218.8	-12
1	60%	40%	PFHxA	11.0	313.0	268.9	-14
			PFHpA	13.7	363.0	318.8	-16
20	10%	90%	PFOA	15.8	413.1	368.9	-14
			PFNA	17.4	463.0	418.9	-16
25	10%	90%	PFDA	18.8	513.0	469.0	-18
			PFBS	8.2	299.0	79.8	-52
26	60%	40%	PFHxS	13.8	399.0	79.9	-74
			PFOS	17.4	499.0	80.1	-84
30	60%	40%	HPFO-DA	11.9	285.1	168.7	-12
			6:2 FTS	15.7	427.1	406.8	-34
			N-EtFOSAA	20.1	584.1	418.8	-30

The curve of the adsorbed mass on the disk in function of the sampling duration was drawn for each molecule (see figure 6). The uptake was observed as linear over the 7 days of the experiment for the 13 molecules. The sampling Rate was calculated for each molecule using the formula below:

$$R_s \text{ (L/days)} = \frac{C_{\text{sampler}} (\mu\text{g/g}) \times M_{\text{sampler}} \text{ (g)}}{C_{\text{tank}} (\mu\text{g/L}) \times \text{time (days)}}$$

The values from day 1 to day 7 were considered for a total of 14 values leading to a mean calculated R_s and a standard deviation value. The results obtained are presented in Table 3.

Table 3 - Sampling rates and standard deviation obtained for the 13 perfluorinated compounds in river water using **AttractSPE® POCIS - PFAS** as passive samplers.

Compound	Mean calculated R_s (L/day)	Standard deviation (n = 14)
PFBA	0.086	0.010
PFPeA	0.136	0.012
PFHxA	0.156	0.013
PFHpA	0.167	0.013
PFOA	0.156	0.012
PFNA	0.155	0.011
PFDA	0.115	0.008
PFBS	0.213	0.017
PFHxS	0.223	0.016
PFOS	0.176	0.032
HPFO-DA	0.181	0.019
6:2 FTS	0.172	0.031
N-EtFOSAA	0.099	0.045

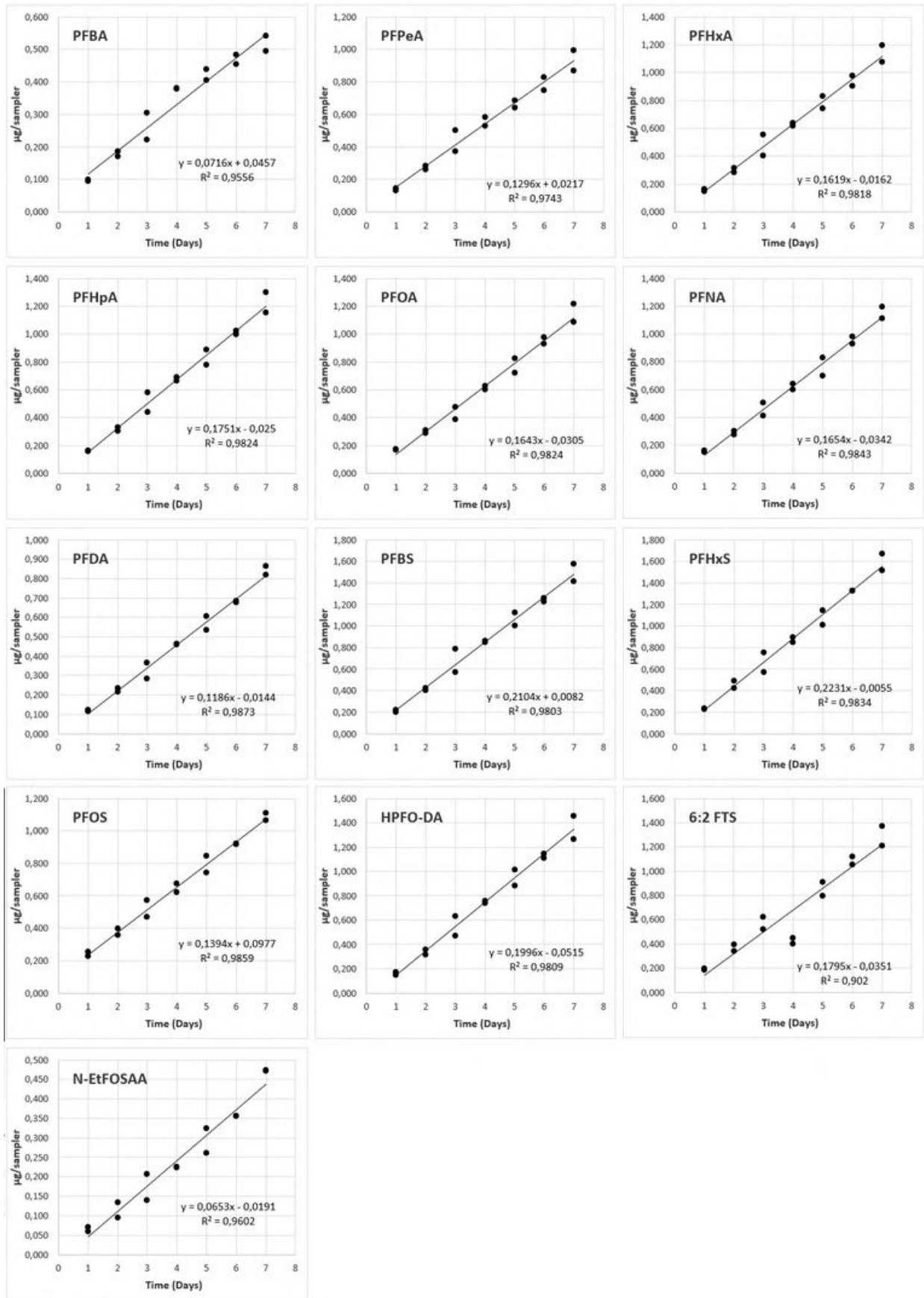


Figure 6. Uptake curve for the 13 molecules measured during the experiment.

Conclusion

AttractSPE® POCIS – PFAS was used to collect 13 perfluorinated compounds. R_s values were measured between 0.086 to 0.223 L/day with a good linearity over the 7 days. Furthermore, the use of **SilactHPLC DELAY - PFAS** as delay column allows to avoid any PFAS interference during LC-MS/MS analysis. Particular attention must be paid to verify that the laboratory environment does not contaminate samples and lead to false positives. Some simple precautionary steps are described in the application note (e.g., the use of a delay column). For routine analysis, the use of internal standards to correct the potential matrix effects and adsorption of the largest PFAS is advised.

References :

1. Impact of Perfluorinated Compounds on Human Health, 2014 Academy for Environment and Life Sciences.

Part number of products used in this application note:

Product:	Quantity:	Part number:
AttractSPE® POCIS - PFAS	10/pk	POCIS.PFAS.90.55.A.10
1 Canister 12 cm + 1 holder 3 position	1/pk	CH-3P.A.1
1 Canister 24 cm + 2 holders 3 position	1/pk	CH-6P.A.1
SilactHPLC LC - PFAS - 150x 2.1mm (3µm) for PFAS analysis	1 unit	LC-PFAS-150.2.1
SilactHPLC DELAY - PFAS - 50x 2.1mm (5µm) for Bisphenol A analysis	1 unit	DELAY-PFAS-50.2.1