

Investigation of legacy and emerging PFAS in wastewater samples through target and suspect screening: an unclosed mass balance

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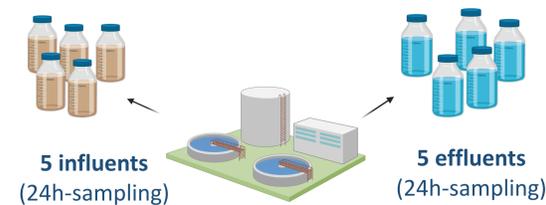
Introduction and aims

Wastewaters can represent a continuous source of PFAS in the environment, and in addition to **legacy PFAS**, **new alternatives and emerging PFAS** may pose additional risks as conventional treatment plants are unable to remove these recalcitrant and persistent compounds.

The assessment of this group of heterogeneous compounds requires an analytical effort that cannot be limited to a target analysis, which is why a **suspect screening** was carried out in parallel with the target analysis in this study, with the aim of fully characterizing the PFAS contamination profile in the influent and effluent of a Belgian urban wastewater treatment plant (WWTP).

Materials and methods

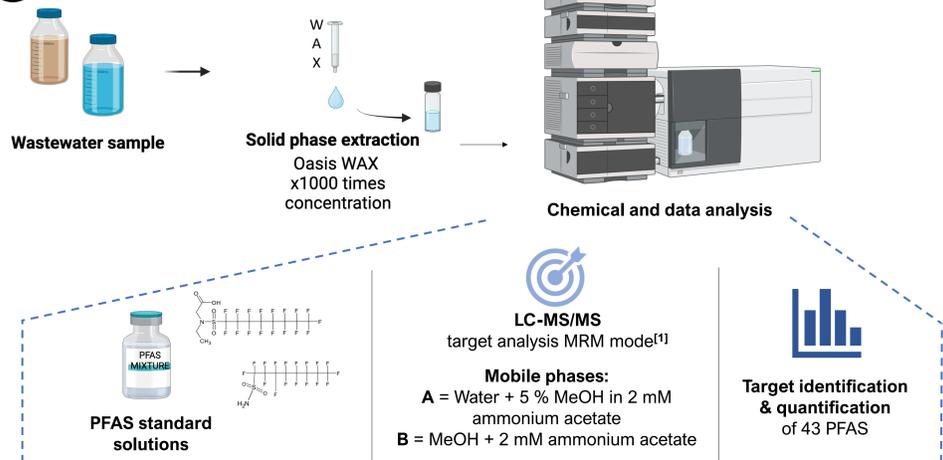
Sampling



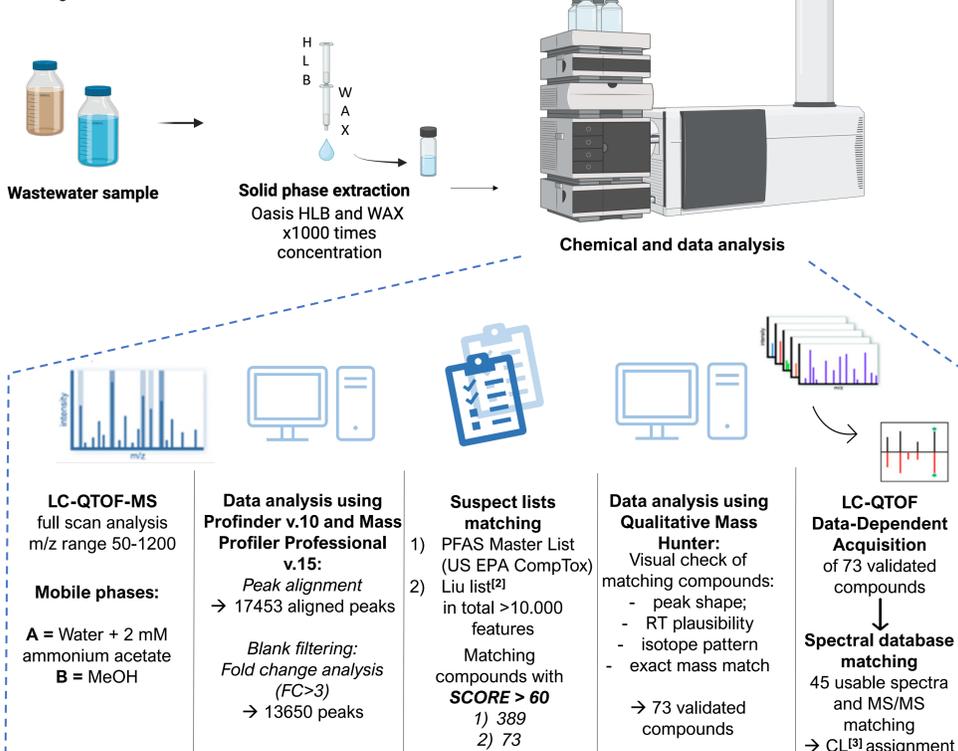
Period: 8/8/2022 – 12/8/2022

WWTP influent quality characteristics			
COD	mg/L	434 ± 151	
TSS	mg/L	257 ± 149	
Total N	mg/L	64 ± 6	
NH ₄ -N	mg/L	49 ± 3	
Total P	mg/L	11 ± 4	
Flow rate	m ³ /day	77.648	
Population equivalent		192.226	

Target analysis



Suspect screening



Results

Target analysis results

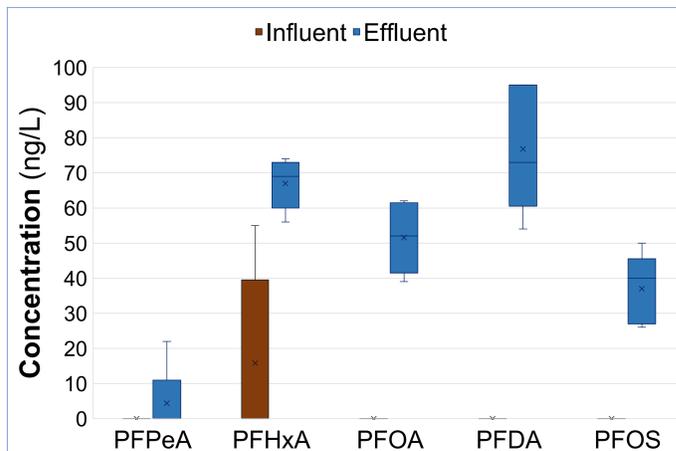


Table 1: Target compounds detected below the LOQ in all the samples.

PFBA	PFOSA
PFHpA	N-MeFOSA
PFNA	N-EtFOSA
PFuDA	N-MeFOSAA
PFDoA	N-EtFOSAA
PFTeDA	8:2 diPAP
PFPeDA	PFTrDA
PFHxDA	PFOcDA
PFBS	PFUnDS
PFPeS	PFDoDS
PFHxS	PFTrDS
PFHpS	PFBSA
PFNS	PFHSA
PFDS	N-MeFBSA
4:2 FTS	N-MeFBSAA
6:2 FTS	6:2 diPAP
8:2 FTS	6:2/8:2 diPAP
10:2 FTS	HFPO-DA
PFECHS	ADONA

- The results of the target analysis showed that in the influents only PFHxA was detected above the LOQ (20 ng/L) and the concentration ranged between <LOQ to 55 ng/L.
- In the effluents, PFPeA, PFHxA, PFOA, PFDA and PFOS were detected in a total concentration range of 188 to 301 ng/L and PFDA was the most predominant.

Suspect screening results and semi-quantification

- The semi-quantification was performed for newly found PFAS identified at confidence level^[3] CL2 (MS² spectra match) and **high-scoring CL4** chemicals, specifically chemicals with a MassHunter Qualitative score >90 (i.e., high isotope pattern and delta mass <5ppm).
- For the semi-quantification, these chemicals were matched with target PFAS according to molecular weight, RT, and functional group **similarity**.
- The ratio of newly identified PFAS peak area divided by that of matched target PFAS was then multiplied by the concentration of the target PFAS quantified. Three concentration ranges were used.

Concentration ranges:

Conc < 10 ng/L
10 < Conc < 100 ng/L
Conc > 100 ng/L

	Chemical name	Acronym	Formula	CAS N°	CL	Occurr INFL	Occurr EFFL	Matching compound	Highest conc. INF (ng/L)	Highest conc. EFFL (ng/L)
1	6:2 Fluorotelomer sulfonamide betaine (Capstone B)	6:2 FTAB	C15H19F13N2O4S	34455-29-3	2a	0 / 5	5 / 5	PFHxS	n.d.	3
2	Perfluorooctanesulfonic acid	PFOSi	C8HF17O2S	647-29-0	2b	0 / 5	5 / 5	PFOS	n.d.	3
3	1:2 H-substituted per-fluoroalkyl ether sulfonate	1:2 H-PFESA	C3H2O4F6S	/	2b	5 / 5	5 / 5	PFBS	23	1
4	2-(Nonafluorobutyl)-4H-1-benzopyran-4-one		C13H5F9O2	304877-96-1	4	2 / 5	0 / 5	PFPeA	25	n.d.
5	4-[(1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Heptafluoronon-1-en-1-yl)oxy]benzene-1-sulfonic acid		C15H5F17O4S	71212-45-8	4	0 / 5	5 / 5	PFOS	n.d.	1
6	4-(1,1,2,3,3,3-Hexafluoropropoxy)-1,1'-biphenyl		C15H10F6O	175838-51-4	4	5 / 5	5 / 5	PFPeA	68	18
7	3-Amino-3-[4-(1,1,2,2-tetrafluoroethoxy)phenyl]propanoic acid		C11H11F4NO3	773122-82-0	4	5 / 5	5 / 5	PFPeA	290	276
8	3,4,4,5,5,6,6,6-octafluorohex-2-enoic acid	4:2 FTUCA	C6H2F8O2	70887-90-0	4	2 / 5	5 / 5	PFPeA	9	11
9	4-(Pentafluoroethyl)-2,3-dihydro-1H-inden-1-one		C11H7F5O	1380390-11-3	4	5 / 5	5 / 5	PFPeA	127	263
10	1,1'-(1,1,2,2-Tetrafluoroethane-1,2-diyl)di(pyrrolidin-2-one)		C10H12F4N2O2	143697-60-3	4	1 / 5	1 / 5	PFPeA	66	5
11	1-(1,3-Dimethylbutoxy)-2-(perfluorohexyl)ethane		C14H17F13O	210896-25-6	4	2 / 5	0 / 5	PFOA	10	n.d.
12	[4-[3-(4-acetyloxyphenyl)-1,1,2,2,3,3-hexafluoropropyl]phenyl] acetate		C19H14F6O4	21250-00-0	4	2 / 5	0 / 5	PFPeA	9	n.d.
13	1,1,1,2,2,3,3,4-Octafluorohexane		C6H6F8	154275-19-1	4	5 / 5	1 / 5	PFPeA	36	1

Conclusions

- Concentrations of target compounds were consistent with those of a previous study^[4] conducted in the influents of the same WWTP in 2020, and the results showed that the concentrations of target compounds were higher in the effluents, resulting in a **negative removal efficiency**.
- The presence of precursors compounds in the influents could explain a higher rate of target PFAS in the effluents, due to the **degradation of precursors** during the treatment processes.
- Suspect screening revealed the presence of emerging PFAS that are precursors** of perfluoroalkyl acids such as the perfluorooctanesulfonic acid (PFOSi) and the 6:2 FTAB (trade name Capstone B), which have been shown to degrade respectively into PFOS and short-chain PFAS like PFBA and PFPeA^[5]. However, the semi-quantification results showed similar concentrations of emerging compounds and not such a marked discrepancy between influents and effluents. This can point out that precursors are in other fractions of material, such as sludges, and that once degraded, the perfluoroalkyl acids go into the effluents. Further investigations, also considering other type of samples, are necessary to close the mass balance and explain the higher rate of PFAS in the effluents.

References

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 [5] D'Agostino & Mabury 2017. 10.1002/etc.3750