Waters™

Application Note

Routine PFAS Testing in Surface Water Using TOP Assay and ACQUITY™ QDa™ II Mass Detector

Henry Foddy, Cristian Cojocariu, Vladimir Nikiforov

Waters Corporation, NILU

Abstract

Per- and polyfluoroalkyl substances (PFAS) have increasingly become a major environmental and public health concern due to their toxic properties and tendency to bioaccumulate in living organisms. Global widespread use of PFAS over many decades has meant that these compounds have become common and persistent environmental pollutants. Traditional testing methods are often challenged to capture the full extent of PFAS pollution; performing a total oxidizable precursors (TOP) Assay analysis allows for the assessment of perfluoroalkyl acid (PFAA) precursors in a given sample, by monitoring perfluoroalkyl carboxylic acid (PFCA) concentrations before and after sample oxidation. Eight surface water river samples were collected downstream from wastewater treatment plants across the northwest of England and analysed using the ACQUITY QDa II Mass Detector. Results demonstrated a marked increase in summed PFCA content in all surface water samples analysed, underlining the utility of such techniques to support and supplement existing PFAS testing methodologies.

Benefits

- TOP Assay offers a means of assessing the burden of perfluoroalkyl acids (PFAAs) as well as their precursors

in a single method, offering a complementary testing approach that can be used to analyse surface water samples

- Utilising the ACQUITY QDa II Mass Detector for this analysis offers a cost-effective, user-friendly, and reliable means of sample triage, using LC-MS and nominal mass information to support and compliment more sophisticated traditional testing methodologies

Introduction

Per- and polyfluoroalkyl substances (PFAS) is a collective name for certain organo-fluorine environmental contaminants, a group synthetic chemicals that have been widely used for decades in a variety of industrial applications and consumer products. Regarded for their durability and resistance to degradation, PFAS have garnered significant attention as a growing environmental and health concern due to their potentially toxic and bio-accumulative properties.[1]

PFAS contamination in rivers, groundwater, and drinking water sources, has been reported globally, with concern expressed that the extent of this contamination is still to be uncovered. In the United Kingdom, this worry has been recently amplified by increasing reports of wastewater and sewage leaks into rivers and other water bodies; this discharge of untreated or partially treated wastewater into rivers can exacerbate trophic transfer and persistence throughout vital ecosystems and food chains.[2] Inherent properties of PFAS such as high persistence, strong sorption, and long-range transportation and deposition, all serve to exacerbate and propagate potential harm to ecosystems.[3] The resistance of PFAS to traditional environmental remediation techniques makes addressing their impacts particularly challenging, necessitating the development of new technologies, and stringent regulatory measures to protect both ecosystems and public health.

The growing awareness of PFAS contamination has placed a significant burden on environmental testing and regulatory frameworks, with traditional testing methods often challenged to capture the full extent of PFAS pollution. Primarily detecting perfluoroalkyl acids (PFAAs), these methods can sometimes overlook potential precursor compounds that can degrade into these persistent substances. Just one of many analytical challenges here includes the lack of authentic standards for the over 12,000 non-PFAA PFAS compounds.[4]

The total oxidizable precursors (TOP) assay offers a means of bridging this gap; by oxidizing the non-fluorinated parts of unknown PFAA precursors and intermediates, and converting them into stable PFAA compounds

offering a broad and more complete insight into the total PFAA burden in environmental samples.[5]

Utilising the ACQUITY QDa II Mass Detector in conjunction with TOP Assay analysis, a cost-effective approach is demonstrated, which can help to alleviate burden on traditional testing methods which are typically more advanced and resource-intensive. This approach serves to complement these traditional approaches, offering additional insight into total PFAS content in a sample, and allowing for more effective triage of potentially contaminated environmental samples.

In this work, several surface water river samples were collected downstream from wastewater treatment plants (WWTPs) across the northwest of England, particularly in areas of noted sewage discharge and overflow a radius of this collection area can be seen in Figure 1.

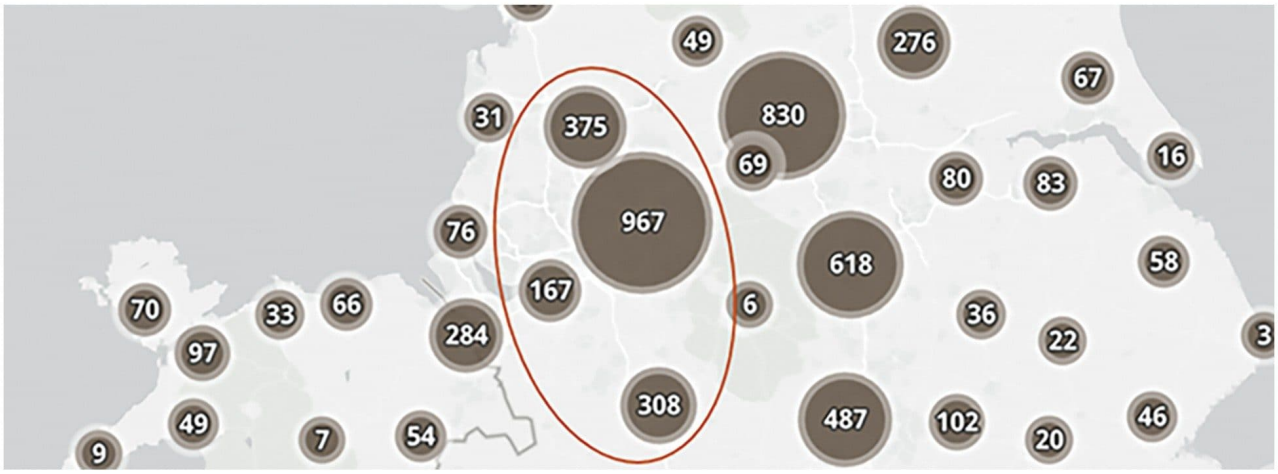

Figure 1. A map denoting sewerage network discharge of treated sewage and overflows of untreated sewage and storm water into rivers in England & Wales in 2023. Source: The Rivers Trust (https://theriverstrust.org/sewage-map). An approximate collection radius of river wastewater samples collected is shown in red.

Experimental

Surface Water Collection

Surface water river samples were collected in June 2024 across various rivers in the northwest of England.

Samples were collected downstream of WWTPs, notably near sites of recently reported sewage discharge or overflow. Approximately 2 litres of sample was collected at each location, using a HDPE container that had previously been rinsed three times with LC-MS grade MeOH, and one time with Milli-Q water. Upon return to the laboratory, samples were filtered and stored at room temperature until analysis, which occurred within 60 days of sample collection.

To monitor any contamination from storage, a blank sample containing 2 litres of Milli-Q water was collected and stored alongside the surface water samples. This reagent water sample was used to prepare a 50 ng/L spiked reagent water sample, which was assessed alongside the surface water river samples.

Total Oxidizable Precursor Assay

The TOP Assay was performed using an approach similar to that described by Houtz and Sedlak,[5] the procedure is detailed in Figure 2. Both control and amended samples were analysed in triplicate. Samples taken through the oxidation procedure are denoted as 'amended' samples throughout the text.

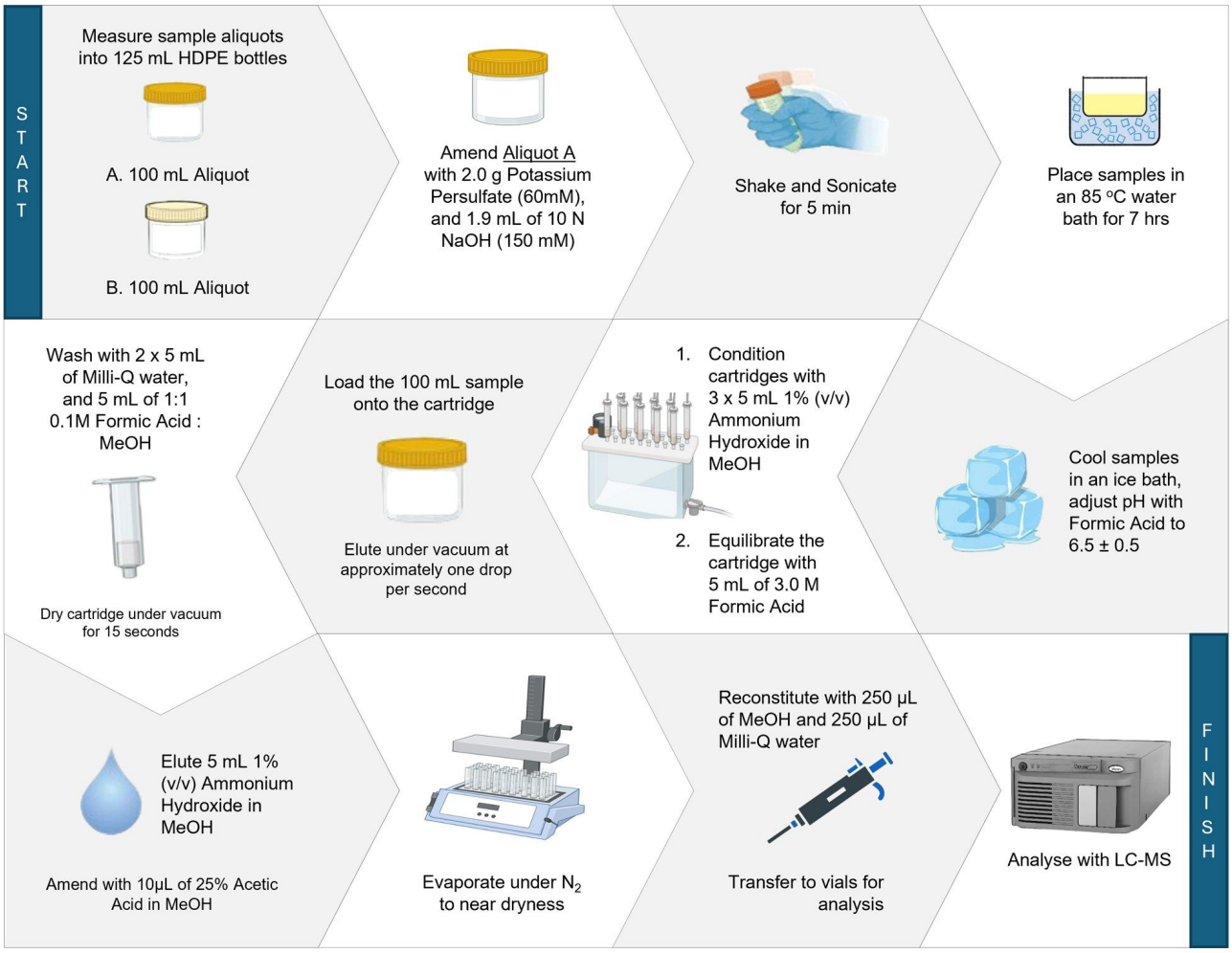

Figure 2. An outline of the sample protocol and solid-phase extraction approach followed in this workflow.

Throughout the procedure, best practices for controlling PFAS contamination in the lab were followed (720007905 <https://www.waters.com/nextgen/global/library/library-details.html?documentid=720007905EN&t=720007905en>). All 125 mL HDPE bottles were washed thoroughly 3x with LC-MS grade MeOH, and once with Milli-Q water prior to use. Once dry, the bottles were labelled and spiked accordingly. Bottles labelled for surface water river samples were spiked with an ADONA solution at a concentration equivalent to 50 ng/L, and a reagent water sample was spiked with a PFAS mix containing ADONA at the same concentration. Subsequently, bottles were allowed to dry in a sample oven for approximately 20 minutes to the evaporate organic solvent.

Following removal from the sample oven, each bottle was placed under gentle nitrogen flow to disperse any remaining vapour that may still be present in the bottles. ADONA is a compound that reliably oxidizes in the TOP Assay procedure and is therefore an indicator of process efficiency. Crucially, it is typically absent in natural surface water samples, and oxidation products do not interfere with analysis.

Prior to SPE, all samples were spiked with an internal standard (IS) mix to assess the efficacy of the extraction procedure. The IS mix was again spiked at 50 ng/L. A further procedural blank was assessed without the IS mix present. Samples were sonicated for 5 minutes prior to extraction. All analytical standards used in this work were obtained from Wellington Laboratories.

Solid-Phase Extraction

Extraction was performed using solid-phase extraction (SPE) with Oasis WAX/GCB cartridges (200 mg WAX, 50 mg GCB) 60 µm WAX particle size (186011111 <https://www.waters.com/nextgen/global/shop/sample-preparation--filtration/186011111-oasis-wax-gcb-for-pfas-analysis-6cc-vac-cartridge-200-mg-wax-50-.html>), following the procedure detailed in the Quick Start Guide (720008199 < https://help.waters.com/help/global/support/library-details.html?documentid=720008199>), with an additional drying step detailed in Figure 2.

Instrumentation

Samples were assessed using the ACQUITY QDa II Mass Detector coupled to an ACQUITY Premier LC equipped BSM with FTN, fitted with a PFAS Kit (176004549 <https://www.waters.com/nextgen/global/shop/application-kits/176004549-pfas-solution-installation-kit--with-oasis-500mg-kit-2.html>). The kit includes an isolator column, that helps to delay any residual background interference that could co-elute with the analytical peak. Resolution, tuning, and calibration are all automated during start-up of the instrument, requiring no analyst intervention. A 22-minute method using an ACQUITY Premier CSH™ C_{18} column was used to provide good separation of the PFAS compounds.

LC-MS Experimental Conditions

LC system:	ACQUITY Premier BSM w/ Flow-Through Needle
Detection:	ACQUITY QDa II Mass Detector

Column(s):	ACQUITY Premier CSH C_{18} Column 1.7 µm, 2.1 x 100 mm (p/n: 186009461)
Column temperature.:	50 °C
Sample temperature.:	10 °C
Injection volume:	10 µL
Flow rate:	0.3 mL/min
Run time:	22 min
Mobile phase A:	2 mM Ammonium Acetate in H_2O
Mobile phase B:	2 mM Ammonium Acetate in Methanol
Vials:	700 µL Polypropylene Screw Cap Vials (p/n: 186005221)
Ionization:	Negative Electrospray (ES-)
Capillary voltage:	0.55 kV
Desolvation temperature:	350 °C
Source temperature:	120 °C
Acquisition mode:	Selected Ion Recording (SIR)

LC Gradient

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.3	95	5	6
1	0.3	75	25	6
6	0.3	50	50	6
13	0.3	15	85	6
14	0.3	5	95	6
17	0.3	5	95	6
18	0.3	95	5	6
22	0.3	95	5	6

Software

Data acquisition, processing, and reporting: MassLynx™ Version 4.2

Results and Discussion

Quantification Of PFCAs as Primary Oxidation Products of PFAS Precursors

Perfluoroalkyl carboxylic acids (PFCAs) are a class of PFAS compounds characterised by a carboxylic acid functional group and a fully fluorinated carbon chain. In the context of the TOP Assay, PFCAs are monitored as the primary oxidation products of PFAS precursors.

Assessing the relative increase in total PFCA concentration following oxidation allows for an estimation of the total burden of oxidizable PFAS precursors present within a given sample, providing a more comprehensive assessment of contamination levels. In this analysis, monitored PFCA compounds were PFBA, PFPeA, PFHpA, PFHxA, PFOA, and PFNA.

In the amended 50 ng/L spiked reagent water sample replicates, PFBA, PFHxA, and PFOA, showed a significant (%) increase in reported concentration compared to control samples of 65%, 67%, and 106% respectively. Conversely, no detectable level of ADONA was observed in any of the amended replicates, indicating complete oxidation in the workflow. A chromatographic comparison of control and amended replicates of the 50 ng/L

spiked reagent water sample can be seen in Figure 3.

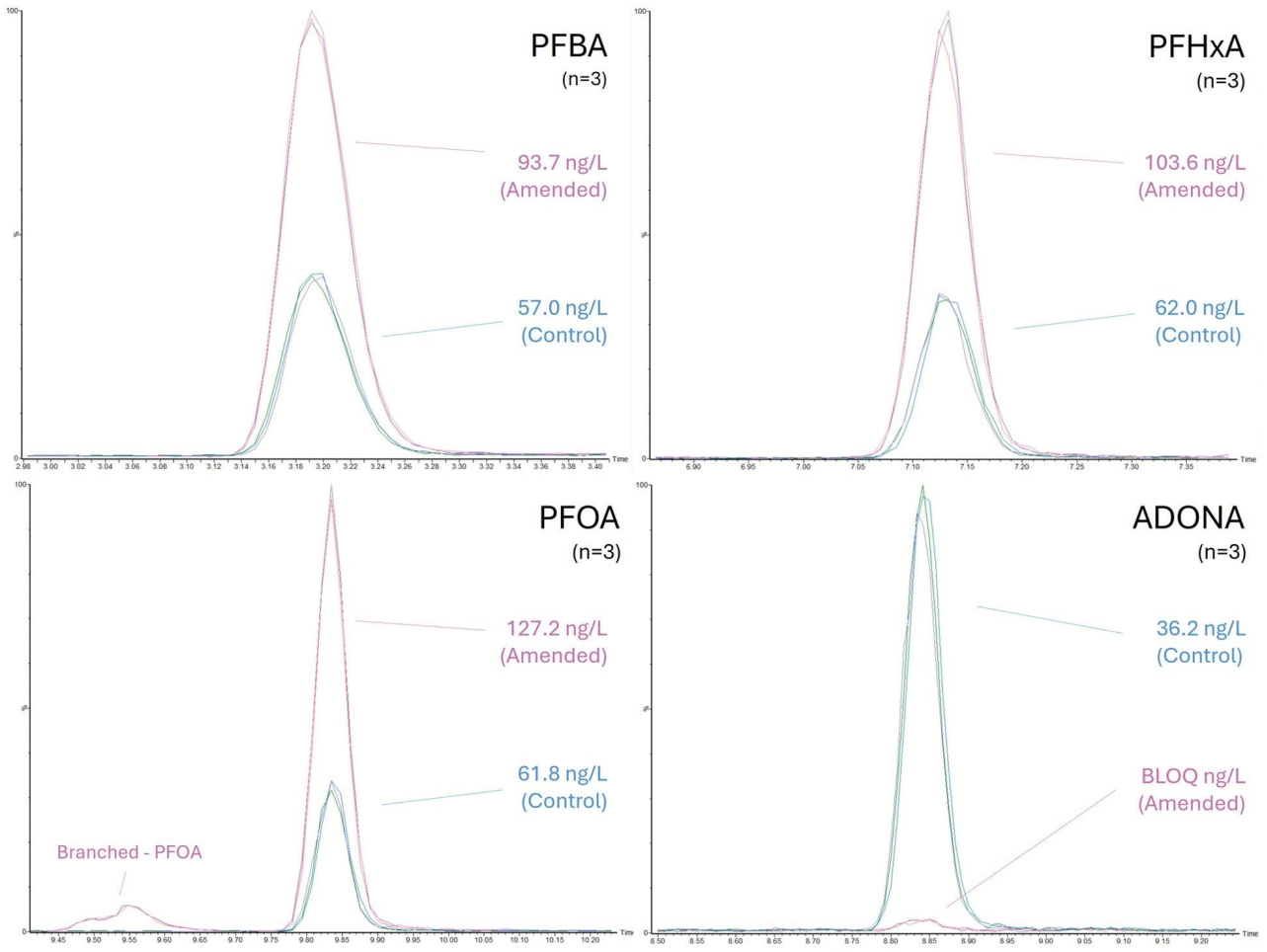

Figure 3. Chromatographic overview of control and amended replicates (n=3) of a 50 ng/L spiked reagent water sample taken through TOP Assay procedure, for PFBA, PFHxA, PFOA, and ADONA.

The increase in select PFCA compounds can be partially explained by the oxidation of other PFAS compounds present in the sample, as can be seen in Figure 4. N-MeFOSAA and N-EtFOSAA reduced in reported concentration by over 90% in the amended samples as compared to control samples, to BLOQ concentrations. Both N-MeFOSAA and N-EtFOSAA have been shown to almost exclusively oxidize into PFOA,[5] which could explain the over two-fold increase in PFOA concentration in the amended samples.[5] Little to no observable change was found in amended concentrations of other PFCA compounds; PFPeA (0%), PFHpA (-4%), and PFNA

(-26%).

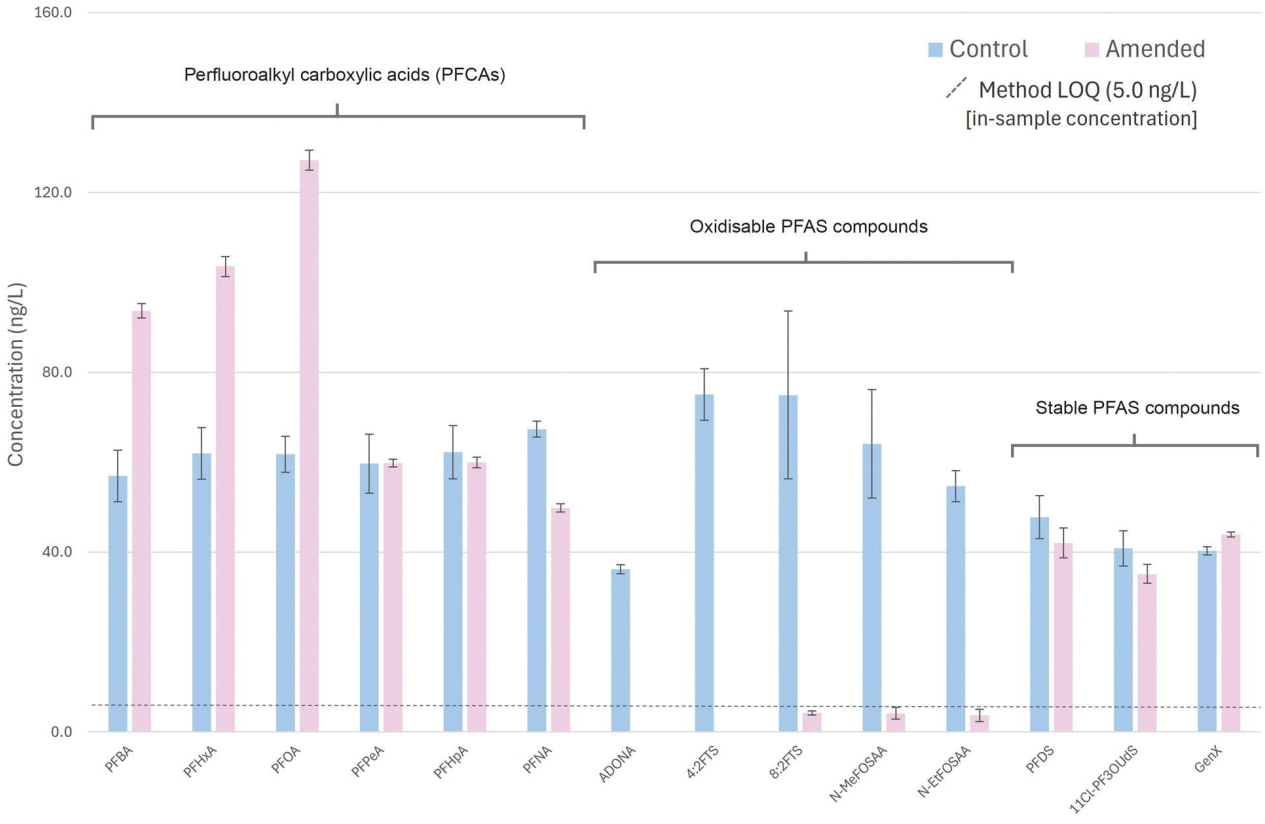

Figure 4. Comparison of calculated concentration of PFAS compounds in control and amended replicates (n=3) of a 50 ng/L spiked reagent water sample taken through TOP Assay procedure. Method LOQ is shown by a dotted line at 5.0 ng/L (in-sample concentration).

No detectable concentration of 4:2FTS was observed in the amended replicates, suggesting complete oxidation. This is expected, as the compound is an oxidizable sulfonic acid. Likewise, concentration of 8:2FTS reduced to BLOQ levels, and reported 6:2FTS concentration reduced by over 90% in amended samples as compared to control replicates, to 7.1 ng/L. Interestingly, degradation of 4:2FTS, 6:2FTS, and 8:2FTS can perhaps be attributed to the increase in respective concentrations of PFBA and PFHxA. In this work, 6:2FTS displayed unacceptable recoveries exceeding 250% in the control spiked replicates; an issue also reported in other TOP Assay analyses.[5] All other monitored PFAS compounds in the 50 ng/L spiked reagent water sample were not oxidizable, and displayed comparable concentrations in the amended replicates as compared to control samples - examples of

which are also shown in the figure below.

All surface water river samples investigated in this work displayed a significant increase in summed PFCA concentration in the amended replicates, as can be seen in Figure 5. Associated values are further detailed in Table 1.

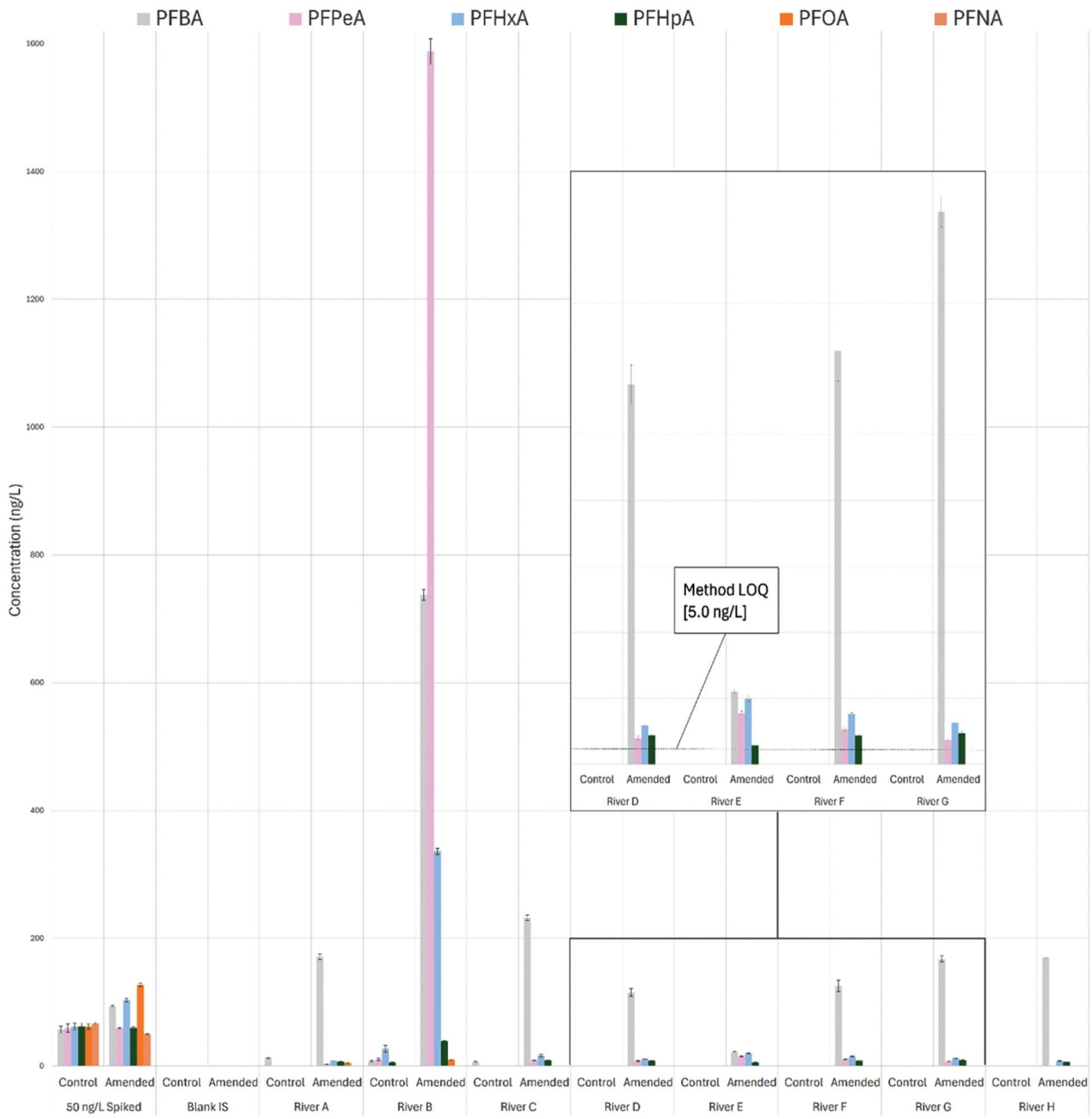

Figure 5. Comparison of PFCA concentration in control and amended replicates (n=3) of surface water samples from Rivers A–H, a 50 ng/L spiked reagent water sample, and a blank sample (with internal standard), taken through TOP Assay procedure. Method LOQ is shown in the inset by a dotted line at 5.0 ng/L (in-sample concentration).

Compound	50 ng/L Spiked		Blank (IS)		River A		River B		River C	
	Control	Amended	Control	Amended	Control	Amended	Control	Amended	Control	Amended
PFBA	57.0	93.7	BLOQ	BLOQ	13.7	171.0	7.7	737.6	6.4	232.1
PFPeA	59.7	59.8	BLOQ	BLOQ	BLOQ	BLOQ	10.3	1588.4	BLOQ	9.3
PFHxA	62.0	103.6	BLOQ	BLOQ	BLOQ	8.6	27.3	336.2	BLOQ	16.2
PFHpA	62.2	60.0	BLOQ	BLOQ	BLOQ	7.3	5.3	39.2	BLOQ	9.5
PFOA	61.8	127.2	BLOQ	BLOQ	BLOQ	5.1	BLOQ	10.0	BLOQ	BLOQ
PFNA	67.4	49.9	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ
Total	**370.0**	**494.1**	**0.0**	**0.0**	**13.7**	**192.0**	**50.6**	**2711.5**	**6.4**	**267.1**
Compound	**River D**		**River E**		**River F**		**River G**		**River H**	
	Control	Amended	Control	Amended	Control	Amended	Control	Amended	Control	Amended
PFBA	BLOQ	115.3	BLOQ	22.0	BLOQ	125.5	BLOQ	167.8	BLOQ	169.8
PFPeA	BLOQ	7.9	BLOQ	15.4	BLOQ	10.6	BLOQ	7.5	BLOQ	BLOQ
PFHxA	BLOQ	11.7	BLOQ	19.9	BLOQ	15.2	BLOQ	12.6	BLOQ	8.4
PFHpA	BLOQ	8.7	BLOQ	5.8	BLOQ	8.7	BLOQ	9.4	BLOQ	6.5
PFOA	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ
PFNA	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ	BLOQ
Total	**0.0**	**143.6**	**0.0**	**63.1**	**0.0**	**160.0**	**0.0**	**197.3**	**0.0**	**184.7**

Table 1. Breakdown of total PFCA concentration reported in control and amended replicates (n=3) of surface water samples from Rivers A–H, a 50 ng/L spiked reagent water sample, and a blank sample (with internal standard) taken through TOP Assay procedure.

Interestingly, the PFCA profiles of oxidized surface water river samples differ to that of the spiked reagent water sample, where PFOA was the most abundant compound post-oxidation. In the majority of surface water river samples investigated, the largest relative increase was found in PFBA, mirroring findings in similar studies.[7,8] This could indicate the presence of perfluoro-butyl substances in the samples.

The River B surface water sample displayed the highest levels of oxidation of all the river samples investigated. One contributing factor could be the level of 6:2FTS observed in the River B control replicates, at an average value of 234.2 ng/L (RSD ±16.9%) (n=3). In many studies, 6:2FTS has been found to be a major PFAS released by WWTPs.[7] 6:2FTS typically oxidizes into PFBA, PFPeA, and PFHxA.[5] The River B sample was also collected at the closest proximity to a WWTP among all samples investigated.

The workflow revealed that although total PFCA content was negligible (BLOQ) in the majority of control river surface water samples, the relative increase following the oxidation procedure in the amended samples suggests the presence of underlying PFCA precursor compounds. Other legacy PFAS compounds monitored were absent

across all control and amended replicates analysed, with the exception of PFOS detected at 6.1 ng/L in the River F control sample.

Two process blank samples were also analysed in this workflow (n=3 technical replicates), to assess any contamination in the sample preparation procedure, as well as any baseline co-elution or contamination that may be present following oxidation. One process blank sample was spiked with an IS mix at a concentration of 50 ng/L. Importantly, both process blank samples with and without IS did not exhibit any detectable level of PFCA concentration in the amended samples.

Likewise, no detectable levels of other monitored PFAS were detected in either the control or oxidized process blank samples, with the exception of 6:2FTS, which was present in the blank (with IS) sample at an average concentration of 67.6 ng/L in the control samples, and 156.6 ng/L in the amended samples. The elevated concentration of 6:2FTS in the amended replicates relative to the control replicates, as well as the absence of any PFCA content in the amended sample replicates, suggests that the compound did not undergo oxidation, and that this contamination was therefore introduced following the oxidation procedure. An example replicate of an amended blank sample (with IS) is shown in Figure 6, demonstrating the absence of monitored PFAS compounds post-oxidation.

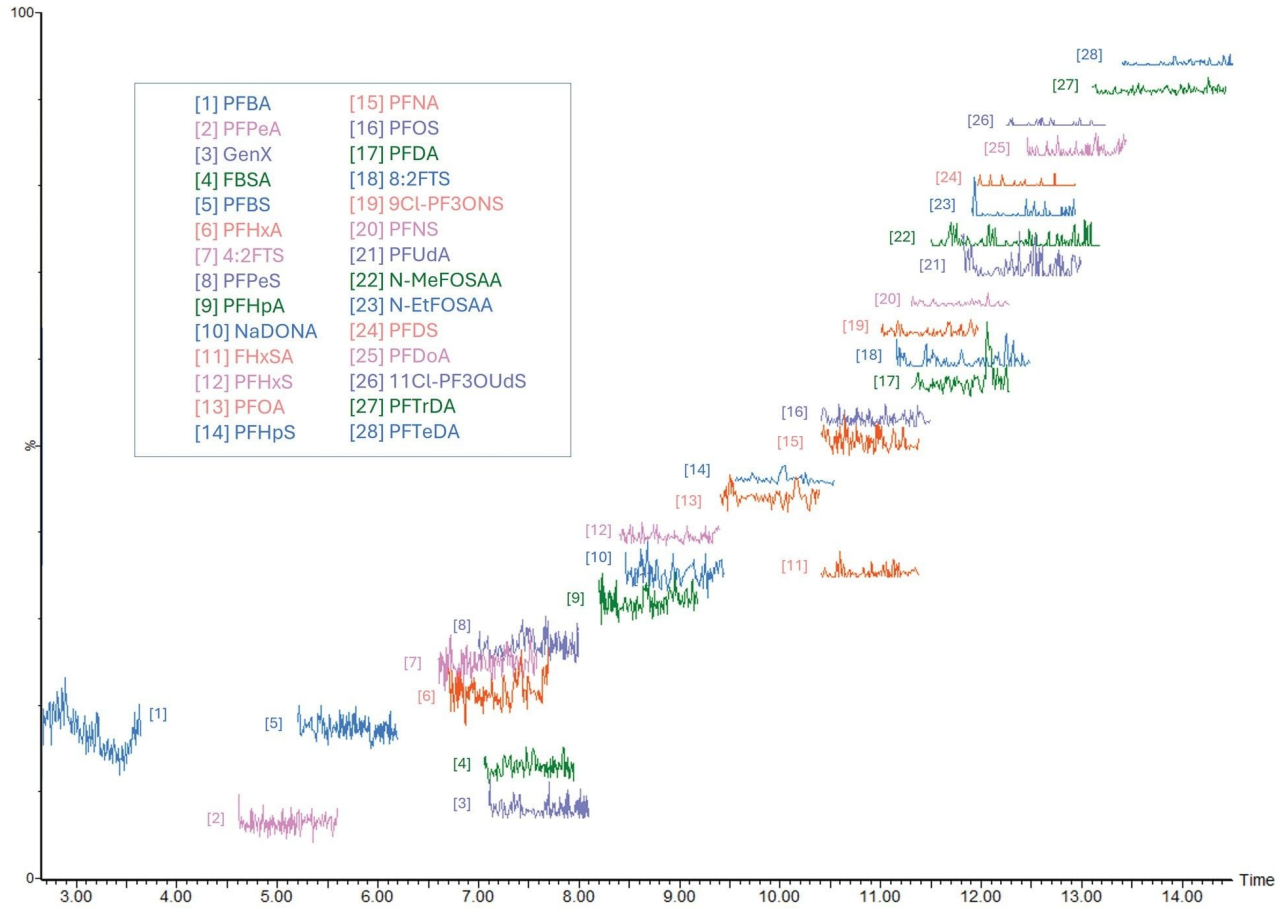

Figure 6. Overview of SIR channels for all monitored PFAS compounds in a procedural blank (with IS) amended replicate, illustrating absence of PFAS compounds in the amended blank samples. [6:2FTS not shown].

In all surface water river samples, ADONA, which was spiked at 50 ng/L, was not detected in any of the amended replicates, indicating successful oxidation (Figure 7). Variation in the concentration of spiked ADONA across surface water samples can be explained, in part, by a lack of internal standard correction for the compound.

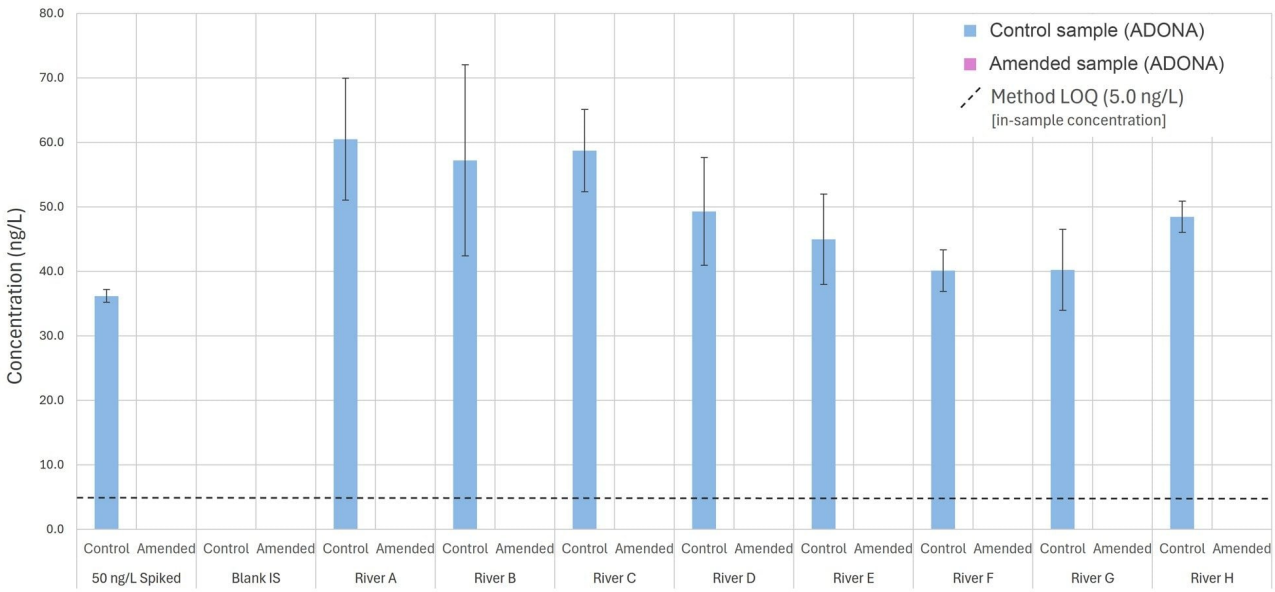

Figure 7. Comparison of ADONA concentration in control and amended replicates (n=3) of surface water river samples following TOP Assay procedure. Method LOQ is shown by a dotted line at 5.0 ng/L (in-sample concentration).

Internal standard recovery was monitored across samples to ensure efficiency of the extraction procedure. PFCA-^{13}C labelled IS recoveries in the blank sample (n=3) ranged from 69–94%, indicating good method performance (Figure 8). Average recoveries across all samples in the workflow (n=30) are detailed in Table 2.

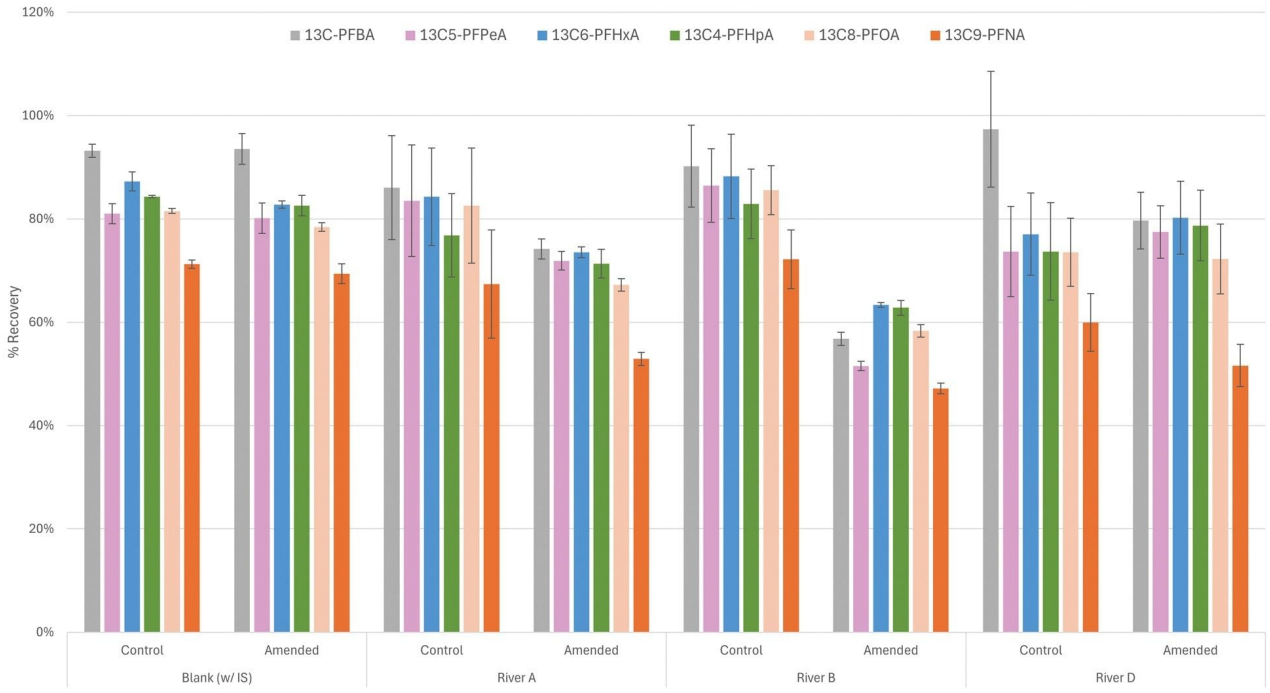

Figure 8. %Recovery of PFCA-13C labelled internal standards across control and amended replicates (n=3) of a blank sample, and representative surface water river samples.

13C-PFBA		13C5-PFPeA		13C6-PFHxA		13C4-PFHpA		13C8-PFOA		13C9-PFNA	
Control	Amended	Control	Amended	Control	Amended	Control	Amended	Control	Amended	Control	Amended
91%	68%	77%	63%	79%	67%	76%	65%	76%	60%	64%	48%

Table 2. Average PFCA-13C labelled internal standard recoveries (%) of both control (n=30) and amended (n=30) replicates across all samples in the analysis.

Sensitivity and Reproducibility

The reproducibility of the data is highlighted in Figure 9, where chromatograms of control and amended triplicate injections (n=3) for PFBA, PFHpA, and PFHxA, in the River A surface water sample are shown. Replicates display concentrations both above and below the method LOQ, given as 5.0 ng/L (in-sample concentration), equivalent to the lowest calibration standard.

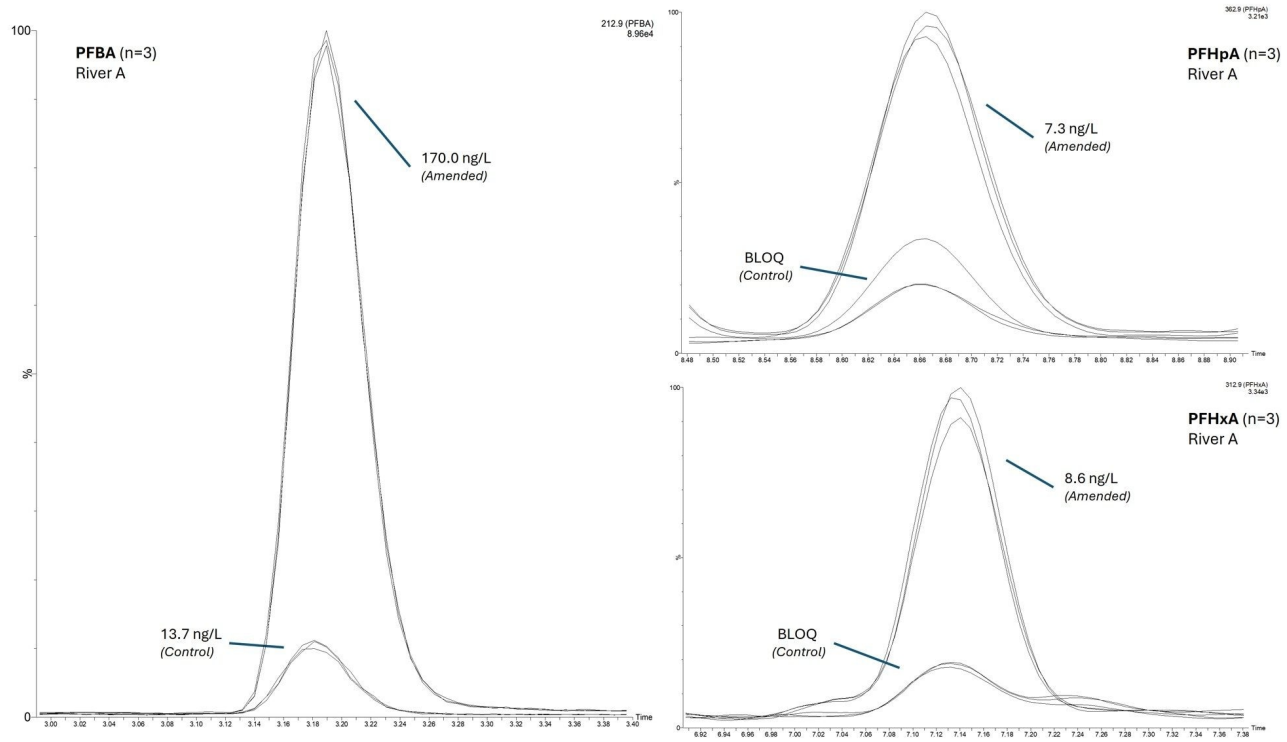

Figure 9. Chromatographic overview of both control and amended replicates (n=3) of the River A surface water sample for PFBA, PFHpA, and PFHxA. Reproducibility across the replicates is shown at levels approaching the method LOQ at 5.0 ng/L (in-sample concentration), demonstrating consistency across the workflow.

Typically, the TOP Assay approach is a qualitative one, however in this workflow samples were bracketed with a calibration curve to better assess method performance. The calibration plot ranged from 1–80 ng/mL (in-vial concentration) for all compounds, (equivalent to 5–400 ng/L in actual sample), spiked with an internal standard mix at 10 ng/mL (equivalent to 50 ng/L in actual sample). R^2 values for all compound calibration plots were >0.99 as seen in supplementary Table S1 (Supplementary Section). Concentrations detailed above this calibration range were subsequently confirmed by further analysis.

Carryover and Instrument Contamination

Solvent injections, comprised of 50:50 MeOH:H_2O were observed throughout the analysis to assess any contamination or carryover in the instrument. No contamination or carryover was observed for any monitored compound throughout the analysis, across all solvent injections. In Figure 10, solvent injections analysed before

and after each surface water sample (n=16) are shown, for all monitored PFCA compounds.

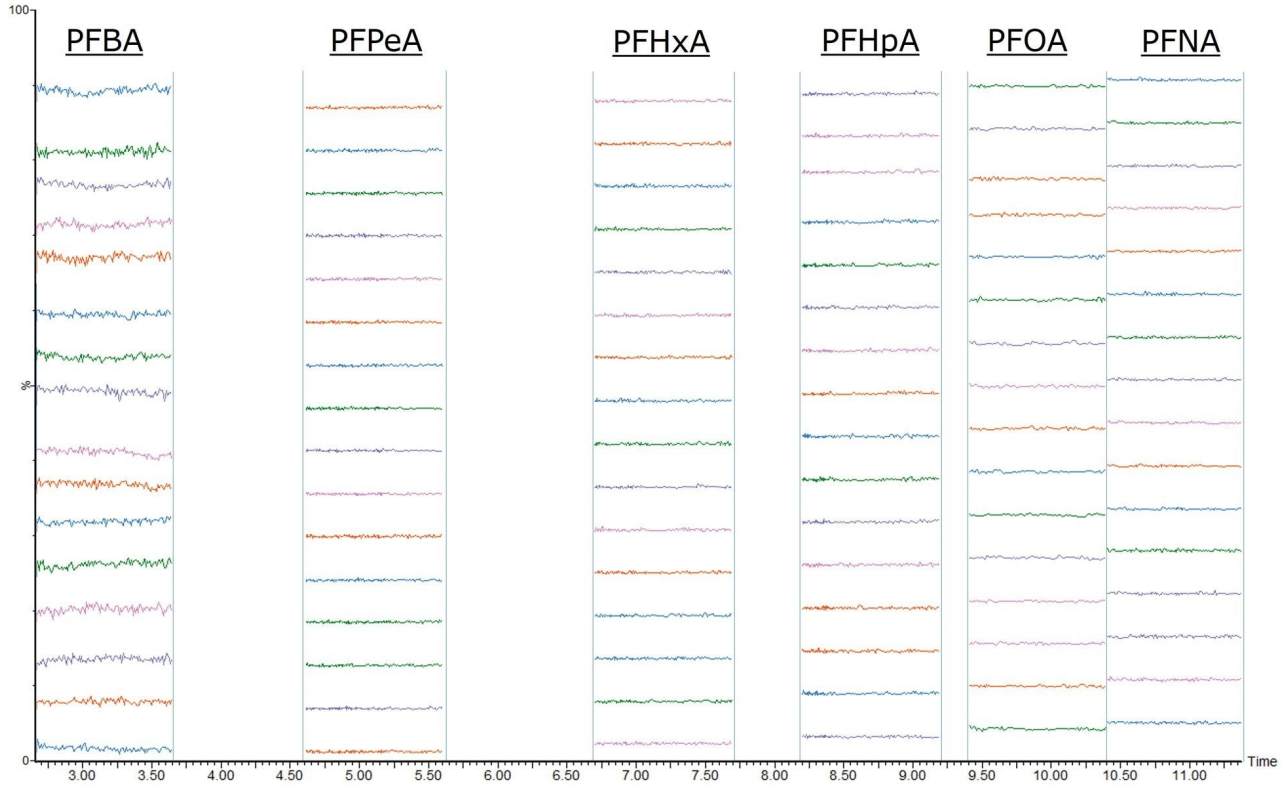

Figure 10. Overview of SIR acquisitions for PFCA compounds in solvent injections (n=16) immediately following and prior to each surface water sample analysed, indicating no system contamination of carryover in the method.

Considerations for TOP Assay Analysis

Using the ACQUITY QDa II Mass Detector, a nominal mass analytical instrument, the scope of PFAS analysis in surface water samples is expanded, demonstrating sufficient sensitivity and reliability to perform this analysis. This approach underlines the utility of additional PFAS workflows, which can help to monitor unknown precursors and unregulated PFAS compounds that could pose significant downstream consequences for local ecosystems and wildlife.

The TOP Assay approach has limitations that should be mentioned; namely that it only encompasses oxidizable

PFAS compounds that degrade and can be detected through targeted analysis.[9] Additionally, HRMS may be needed to confirm concentrations of PFBA and PFPeA due to potential matrix interferences and false positives during oxidation. However, both control and amended samples prepared through TOP Assay can be re-analysed directly with HRMS or LC-MS/MS without the need to repeat sample preparation. For samples requiring the highest sensitivity in ultra-trace quantification and confirmation of PFAS, more sensitive instrumentation such as the Xevo™ TQ Absolute™ should be used.[10]

Conclusion

Quantifiable increases in at least three of the six monitored PFCA compounds were observed in all surface water river samples examined in this workflow. This suggests a large presence of PFAA precursors or other unknown PFAS compounds within the samples, that otherwise may not have been fully captured, warranting further investigation. Large concentrations of PFBA were observed post-oxidation across most samples, suggesting that perfluoro-butyl precursors are the main type of PFAS precursors in the local rivers assessed.

- By comparing PFCA concentrations before and after oxidation, the TOP Assay can reveal the extent of "hidden" PFAA precursors that traditional PFAS workflows may not fully capture, therefore enhancing a laboratory's detection capabilities
- All eight surface water river samples tested showed a significant increase in total PFCA content following oxidation, with levels ranging from 63 to 2711 ng/L (ppt). This indicates a high degree of precursor contamination that legacy analysis may have overlooked
- The ACQUITY QDa II Mass Detector is well-suited to this workflow, providing nominal mass data in a reliable and cost-effective LC-MS analysis, for complementary sample assessment
- Effective triage of potentially contaminated environmental samples can help to support traditional LC-MS/MS PFAS testing methodologies

References

1. Podder, A. *et al.* (2021) 'Per and poly-fluoroalkyl substances (PFAS) as a contaminant of emerging concern in

Surface Water: A transboundary review of their occurrences and toxicity effects', *Journal of Hazardous Materials*, 419, p. 126361. doi:10.1016/j.jhazmat.2021.126361 <https://pubmed.ncbi.nlm.nih.gov/34157464/> .

2. Junaid, M. *et al*. (2024) 'Trophic transfer and interfacial impacts of micro(nano)plastics and per-and polyfluoroalkyl substances in the environment', *Journal of Hazardous Materials*, 465, p. 133243. doi:10.1016/j.jhazmat.2023.133243 <https://www.semanticscholar.org/paper/Trophic-transfer-and-interfacial-impacts-of-and-in-Junaid-Liu/185546c9e1eed1f2c9ca7a28fd6e34395b304609> .

3. Wee, S.Y. and Aris, A.Z. (2023) 'Environmental impacts, exposure pathways, and health effects of PFOA and PFOS', *Ecotoxicology and Environmental Safety*, 267, p. 115663. doi:10.1016/j.ecoenv.2023.115663 < https://pubmed.ncbi.nlm.nih.gov/37976959/> .

4. U.S. EPA. PFAS Strategic Roadmap: EPA's Commitments to Action 2021–2024. https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024 < https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024> (Accessed: 16 August 2024).

5. Houtz, E.F. and Sedlak, D.L. (2012) 'Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff', *Environmental Science & Technology*, 46(17), pp. 9342–9349. doi:10.1021/es302274g < https://pubs.acs.org/doi/10.1021/es302274g> .

6. Zhang, C. *et al*. (2019) 'Fate of per- and polyfluoroalkyl ether acids in the total oxidizable precursor assay and implications for the analysis of impacted water', *Environmental Science & Technology Letters*, 6(11), pp. 662–668. doi:10.1021/acs.estlett.9b00525 <https://pubs.acs.org/doi/10.1021/acs.estlett.9b00525> .

7. van Hees, P, 2017. Analysis of the unknown pool of PFAS: Total Oxidizable Precursors (TOP), PFOS Precursor (PreFOS), and Telomer Degradation. *Eurofins Environment Testing Sweden AB and Man-Technology-Environment Research Centre*, Örebro University.

8. Ye, F., Tokumura, M., Islam, M. S., Zushi, Y., Oh, J., Masunaga, S. Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent. Case study of Tama River, Japan. *Wat. Res.,* 2014, 67, 77–85.

9. Rehnstam, S., Czeschka, M.-B. and Ahrens, L. (2023) 'Suspect screening and total oxidizable precursor (TOP) assay as tools for characterization of per- and polyfluoroalkyl substance (pfas)-contaminated groundwater and treated landfill leachate', *Chemosphere*, 334, p. 138925. doi:10.1016/j.chemosphere.2023.138925 <

https://pubmed.ncbi.nlm.nih.gov/37187375/> .

10. K Organtini, H Foddy, N Dreolin, *S* Adams, K Rosnack, P Hancock. Ultra-Trace Detection of Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water to Meet New US EPA Interim Health Advisory Levels. Waters Application Note. 720007855 <https://www.waters.com/nextgen/global/library/application-notes/2023/ultra-trace-detection-of-per--and-polyfluoroalkyl-substances-pfas-in-drinking-water-to-meet-new-us-epa-interim-health-advisory-levels.html> . 2023.

Supplemental Material

List of compounds	ESI	*m/z*	CV	Calibration range (ng/mL)		R^2	Calibration (1/X)	Linked internal standard
PFBA	-ve	212.9	5	1	80	0.994	Linear	13C-PFBA
PFPeA	-ve	262.9	5	1	80	0.996	Linear	13C5-PFPeA
GenX	-ve	285.0	20	1	80	0.990	Linear	n/a
FBSA	-ve	297.9	20	1	80	0.994	Linear	13C4-PFHpA
PFBS	-ve	298.9	25	1	80	0.993	Linear	13C3-PFBS
PFHxA	-ve	312.9	5	1	80	0.994	Linear	13C6-PFHxA
4:2FTS	-ve	326.9	25	1	80	0.995	Quadratic	13C2-4:2 FTS
PFPeS	-ve	348.9	25	1	80	0.992	Linear	13C3-PFHxS
PFHpA	-ve	362.9	5	1	80	0.994	Linear	13C4-PFHpA
FHxSA	-ve	398.0	20	1	80	0.994	Linear	13C4-PFHpA
ADONA	-ve	376.9	5	1	80	0.992	Quadratic	n/a
PFHxS	-ve	398.9	25	1	80	0.994	Linear	13C3-PFHxS
PFOA	-ve	412.9	5	1	80	0.996	Linear	13C8-PFOA
6:2FTS	-ve	426.9	30	1	80	0.998	Quadratic	13C2-6:2 FTS
PFHpS	-ve	448.9	35	1	80	0.995	Linear	13C8-PFOS
PFNA	-ve	462.9	10	1	80	0.997	Linear	13C9-PFNA
PFOS	-ve	498.9	40	1	80	0.993	Linear	13C8-PFOS
PFDA	-ve	512.9	10	1	80	0.995	Linear	13C6-PFDA
8:2FTS	-ve	526.9	35	1	80	0.990	Quadratic	13C2-8:2 FTS
9Cl-PF3ONS	-ve	530.9	25	1	80	0.995	Linear	13C8-PFOS
PFNS	-ve	548.9	40	1	80	0.993	Linear	13C8-PFOS
PFUdA	-ve	562.9	5	1	80	0.995	Linear	13C7-PFUnDA
N-MeFOSAA	-ve	569.9	25	1	80	0.991	Linear	D3-N-MeFOSAA
N-EtFOSAA	-ve	583.9	20	1	80	0.991	Linear	D5-N-EtFOSAA
PFDS	-ve	598.9	45	1	80	0.990	Linear	13C8-PFOS
PFDoA	-ve	612.9	5	1	80	0.994	Linear	13C-PFDoDA
11Cl-PF3OUdS	-ve	630.9	35	1	80	0.996	Linear	13C9-PFNA
PFTrDA	-ve	662.9	10	1	80	0.993	Linear	13C-PFDoDA
PFTeDA	-ve	712.9	10	1	80	0.992	Linear	PFTreDA

Table S1. Summary of monitored PFAS compounds.

Featured Products

ACQUITY Premier System <https://www.waters.com/nextgen/global/products/chromatography/chromatography-systems/acquity-premier-system.html>

Xevo TQ Absolute Triple Quadrupole Mass Spectrometry <https://www.waters.com/nextgen/global/products/mass-spectrometry/mass-spectrometry-systems/xevo-tq-absolute.html>

MassLynx Mass Spectrometry Software <https://www.waters.com/nextgen/global/products/informatics-and-software/mass-spectrometry-software/masslynx-mass-spectrometry-software.html>

ACQUITY QDa II Mass Detector <https://www.waters.com/nextgen/global/products/mass-spectrometry/mass-spectrometry-systems/acquity-qda-ii-mass-detector.html>

720008648, December 2024

© 2025 Waters Corporation. All Rights Reserved.
Terms of Use Privacy Policy Trademarks Careers Legal and Privacy Notices Cookies Cookie Preferences