Aqueous leaching of ultra-short chain PFAS from (fluoro)polymers: Targeted and non-targeted analysis

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ABSTRACT

Fluoropolymers are a class of per- and polyfluoroalkyl substances (PFAS) defined as high molecular weight plastics containing only carbon-based backbones with F-atoms directly attached. Here, we used targeted and non-targeted analytical methods to quantify aqueous leaching of small molecule PFAS from three types of fluoropolymer and three types of non-fluorinated polymer tubing material. C_2-C_4 perfluoroalkyl carboxylic acids (PFCAs) were quantified with ion chromatography-mass spectrometry, C_4-C_9 PFCAs were quantified with liquid chromatograph-tandem mass spectrometry. A new ^{19}F NMR method with lower detection limits provided an unbiased, non-targeted view of all fluorinated chemicals in the aqueous leachate. C_2-C_4 had higher concentration than longer chain PFCAs. All tubing tested, including non-fluorinated polymers, contained trifluoroacetic acid (C_2 PFCA) above the blank. NMR identified additional fluorinated chemicals, especially in the non-fluorinated PEEK, a common replacement for fluoropolymers in laboratory chromatography systems. Overall, each fluoropolymer tested had different fingerprints of C_2-C_4 PFCA which may be related to their synthetic production such as processing aids, residuals, and inhibitors used; fluorinated chemicals were also identified from non-fluorinated polymers. The outcome of this work informs better trace analysis in the lab and presents an indication on how fluoropolymers and other plastics can be an emission source to the environment.

KEYWORDS

Fluoropolymers

PFAS

Aqueous environment

Lab artifacts Ion chromatography

Nuclear magnetic resonance

SYNOPSIS

Laboratory tubing materials release PFAS into water, with fluoropolymers generally releasing more PFAS than nonfluorinated polymers, especially ultra-short chain PFAS like trifluoroacetic acid.

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals grouped by the presence of one or more perfluoroalkyl carbon atom(s).[1] Due to the high persistence, bioaccumulation potential, toxicity, and/or mobility potential of some specific PFAS, the entire class has been flagged as potentially concerning,[2] with a need to understand the effects of all PFAS. Within PFAS, there are polymeric and non-polymeric PFAS, the latter of which are more thoroughly investigated for their environmental impacts. Polymeric PFAS are further divided into side-chain fluorinated polymers, perfluoropolyethers, and fluoropolymers.[3] Fluoropolymers, which are the focus of the present study, are high molecular weight solid plastics containing only carbon-based backbones with F atoms directly attached to them based on the (co)polymerization of olefinic monomers, where one or more monomer has F bound to at least one of the olefinic C atoms.[3] Fluoropolymers are used in plastic and rubber manufacturing, added to coatings, paints, lubricants and greases, and used in the chemical industry,[4] including in laboratory materials and equipment. Manufacturers argue fluoropolymers are "polymers of low concern" due to their high stability;[5] however, their synthesis often requires the usage and emission of non-polymeric PFAS used as processing aids and starting materials, and their residuals are not fully characterized.[6] Additionally, the high persistence of fluoropolymers is a concern in itself, as plastic persistence in the environment leads to global pollution.

Ultra-short chain perfluorocarboxylic acids (PFCAs, C_2-C_4) are ubiquitous environmental contaminants with poorly understood environmental sources.[7,8] Recent reports of the C_2 PFCA, trifluoroacetic acid (TFA), in archived or dated samples show dramatic increases, especially over the past 20 years through measurements in ice cores,[9] leaves,[10] and surface water.[11] Recently, TFA and other ultra-short chain PFCAs were reported as the predominant PFAS in several matrices

such as drinking water and dust from the USA.[12] During our research on these contaminants, we identified our own laboratory materials as a contamination source. While PFAS contamination has been observed in many laboratory materials, standard analytical methods have not allowed characterization of ultra-short chain PFCAs due to high water solubility and therefore poor retention on C18 columns, and ubiquitous background contamination.[13] Progress by our groups and others using ion chromatography-mass spectrometry and ^{19}F NMR[14–16] now enable these measurements.

Side-chain fluorinated polymers[17–20] and directly fluorinated HPDE[21,22] have been identified as sources of small molecule PFAS like PFCAs, but fluoropolymers as sources of small molecule PFAS is less understood. Evidence from the PFAS research community suggests fluoropolymers may be sources of small molecule PFAS due to, for example, the need for delay columns in HPLC systems and avoidance of polytetrafluoroethylene (PTFE) septa on autosampler vials.[23] In the atmospheric chemistry community, researchers identified interferences caused by TFA, C_3 PFCA (perfluoropropanoic acid, PFPrA) and other PFCAs off-gassing from fluoropolymer inlets.[24,25] Under extreme temperatures (~ 400°C and higher), PTFE forms a range of PFCAs,[26,27] and the C_8 PFCA, perfluorooctanoic acid (PFOA), was measured in high concentrations in fluoropolymer raw materials and finished products under extreme temperatures.[28] Small molecule PFAS have been measured in personal care products that have PTFE listed on their labels, but the authors did not look for TFA and PFPrA.[29,30]

Despite the knowledge described above, quantitative, systematic studies have not been performed to characterize small molecule PFAS originating from fluoropolymers. The objective of this work was thus twofold: to identify possible sources of ultra-short chain PFCA laboratory contamination from fluoropolymers, and to identify additional uncharacterized sources of ultra-

short chain PFCAs to the environment. We also aimed to identify other small molecule organofluorine chemicals from polymers using a nontargeted approach. We hypothesized that TFA, PFPrA, and C_4 PFCA (perfluorobutanoic acid, PFBA), would leach from fluoropolymers into water, while non-fluorinated polymers would not be a source of these chemicals. Three types of fluoropolymer tubing (PTFE, perfluoroalkoxy alkanes – PFA, fluorinated ethylene propylene – FEP) and three types of non-fluorinated polymer tubing (polyvinyl chloride – PVC, polypropylene – PP, polyether ether ketone – PEEK) were tested by aqueous extraction. Targeted analysis was performed with IC-MS and ultra-high performance liquid chromatography – tandem mass spectrometry (LC-MS/MS), and non-targeted with ^{19}F NMR.

2. MATERIALS AND METHODS

2.1 Experimental setup and sampling

PTFE, PFA, FEP, PVC and PP tubing was purchased from McMaster-Carr, while PEEK tubing was purchased from Waters (details in SI). Specific details of manufacturing, processing, and material handling were unavailable despite our best efforts. Chemical details are described in the SI.

Accurately weighed tubing samples were added to 15 mL conical polypropylene tubes using care to avoid lab-related contamination. Then, 10 mL of deionized water (DIW, 18.2 MΩ·cm) produced from a Millipore Direct 8 system was added to each tube, ensuring samples were completely submerged. For tubing samples analyzed via IC-MS, experiments used 3 replicate pieces extracted sequentially via sonication at room temperature 3 times, for 60 minutes each using a Branson 8510 sonicator bath at room temperature. For NMR, an experiment with one larger piece was sonicated once, for 180 minutes. This NMR sample was also injected on UHPLC-MS/MS for comparison.

For all experiments, laboratory blanks were performed using the same water as used for samples (details in SI). PEEK was not available for the IC-MS experiments and was only subject to NMR and UHPLC-MS/MS.

2.2 Analytical methods

Three complimentary methods were used: 1) IC-MS; 2) ^{19}F NMR; and 3) UHPLC-MS/MS. Full analytical method details can be found in the SI.

2.2.1 IC-MS analysis.

TFA, PFPrA, and PFBA were quantified using suppressed IC-MS with a quadrupole MS. Samples were diluted with $^{13}C_2$ TFA and $^{13}C_3$ PFBA and injected directly into the system. Analytes passed through a concentrator column before separation using anion exchange under a NaOH gradient and MS analysis in electrospray ionization negative mode. Sample chromatograms, including inter-injection variability are shown in the SI (Figure S1-S4).

2.2.2 ^{19}F NMR analysis.

For this experiment, 4 sections of 4 cm of each tubing type were cut and placed into a 15 mL conical tube, and extracted with 10 mL DIW once, with 3 hours of sonication. There was only one replicate per tubing type given the NMR acquisition time. Samples were spiked with internal standard 4,4'-difluorobenzophenone (4,4'-DFB, most samples) or 4,4,4-trifluoro-1-butanol (PEEK tubing sample only) in D_2O prior to analysis. ^{19}F NMR was acquired using a previously described noise-reduction acquisition strategy[14] on a 600 MHz probe. Representative spectra are shown in Figures S1-S4.

2.2.3 UHPLC-MS/MS analysis

The same samples analyzed by NMR (n=1 per polymer type) were spiked with mass labelled internal standard (C_4-C_9 from Wellington Laboratories) and analyzed using a method previously described.[14]

RESULTS AND DISCUSSION

The fluoropolymers tested overall contained higher concentrations of ultra-short chain PFCAs than non-fluorinated polymers; however, non-fluorinated polymers were not PFCA-free. After three 1-hour extractions into water, TFA, PFPrA and PFBA were quantified using IC-MS. TFA was measured above the blank in all samples, with the highest summed polymer concentrations of 121 ± 96 ng/g from FEP tubing (Figure 1). One PFA tubing sample, "PFA1" contained the second highest amount of TFA with 34.6 ± 11.6 ng/g. FEP is a co-polymer of tetrafluoroethylene and 12-14% hexafluoropropylene (F_2C=$CFCF_3$) and is less efficient at co-polymerization than PFA.[31] Excess hexafluoropropylene may create residual TFA, as upon atmospheric oxidation, hexafluoropropylene forms CF_3COF in 100% yield, which will hydrolyze to form TFA.[32] Additionally, non-fluorinated tubing PVC1 contained higher TFA levels than some of the fluoropolymers sampled, such as PTFE. PFPrA was highest in PFA samples at 11.5 ± 6.8 and 16.0 ± 15.4 ng/g. Surprisingly, the PP sample contained higher levels of PFPrA than PTFE, within error of FEP. Some PFAS have applications as mold release agents for plastic production, including for PP, but PFPrA itself has not been identified to have that application.[4] Both PTFE samples contained high concentrations of PFBA, at 175 ± 298 ng/g and 71.3 ± 79.4 ng/g for PTFE1 and PTFE2. The triplicate pieces extracted show a large spread in PFBA concentration. Based on

our data on inter-injection reproducibility, we are confident this is not an instrumental artefact (see SI Figure S4). This heterogeneity suggests PFBA may be a residual from polymer processing.[31] Levels of PFBA are at least 20x greater than measured in a previous study of fluoropolymer raw materials and products made in China (TFA and PFPrA were not measured).[28]

By examining sequential extractions, it was possible to assess whether fluoropolymers could be pre-treated to avoid laboratory contamination. TFA concentrations decreased after each extraction (Figure 1). PFBA was effectively removed after the first extraction, which supports our hypothesis that it may be a residual. PFPrA was not effectively cleaned, as extract 3 contained more PFPrA than extract 2 for most polymers. The blank concentration of PFPrA was consistent across all extractions, so we hypothesize that the increase was caused by sonication changing the polymer structure and releasing additional PFPrA from within the polymer. The concentration of PFPrA was highest in PFA samples, and the third extract being more concentrated than the second was also most prominent in the PFA samples. PFA is a co-polymer of tetrafluoroethylene and perfluoroalkyl vinyl ethers, often perfluoropropyl vinyl ether ($C_3F_7OCF=CF_2$).[33] Perfluoropropyl vinyl ether is efficiently oxidized to PFPrA under ambient atmospheric conditions.[34] Another potential source is perfluoropropionyl peroxide inhibitors (e.g. bis(pentafluoropropionyl) peroxide, $C_2F_5C(O)OOC(O)C_2F_5$, CAS 356-45-6) that are used during the co-polymerization of PFA in fluorinated solvents.[33]

From our experience working with PFPrA experiments and environmental samples, we have noticed its behavior with respect to blank contamination and reproducibility is different than other PFCAs, but given the limited measurements of PFPrA, this has not been thoroughly documented. Another challenge with PFPrA is that there is not a commercially available isotopically labelled PFPrA (note: since this work was performed, we have become aware of a

recently released ^{13}C PFPrA); here, we used $^{13}C_3$ PFBA for our IC-MS analysis as the retention times for PFPrA and PFBA were more similar than PFPrA and TFA. Very few measurements exist of PFPrA in the environment, and its fate is not well understood, however, it was observed as a common contaminant in drinking water in the USA and Germany. [8,12,35]

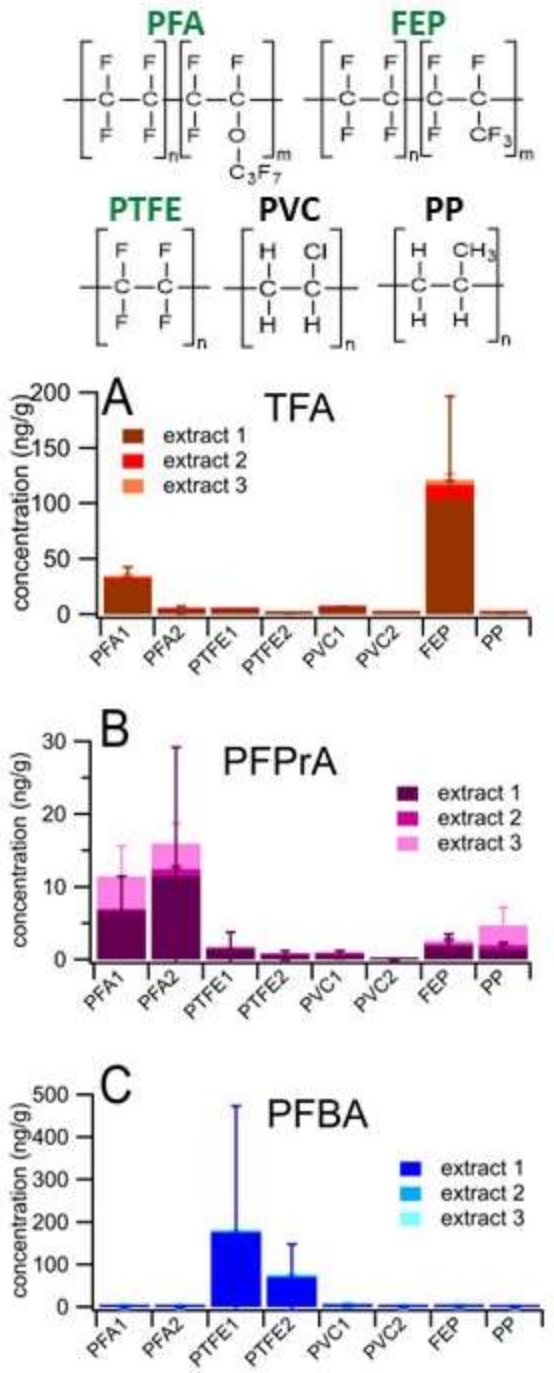


Figure 1. Sequential 1-hour extractions of ultra-short-chain PFCAs from tubing into water, quantified with IC-MS. Here, data from each extraction was averaged across triplicate tubing samples, with error bars representing standard deviation. Concentrations from sequential extracts are stacked.

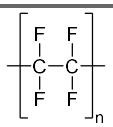
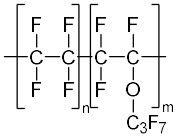
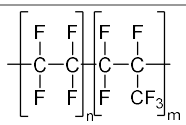
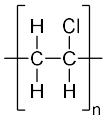
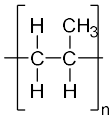
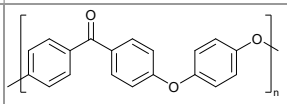
For an unbiased, non-targeted view of all fluorinated chemicals in the aqueous leachate of the tubing, ^{19}F NMR was performed using a new method with lower detection limits than previously available for this instrument.[14] Concentrations of identifiable resonances were calculated through integral area comparison with the internal standard. The blank showed only a small concentration of F^- at -121 ppm indicating no significant contamination of organofluorine in the source water used for extraction. In all samples measured by both IC-MS and NMR, similar concentrations of ultra-short chain PFCAs were measured (data in SI). In the PFA1 sample, concentrations of both TFA and PFPrA align with targeted IC-MS method and no additional organofluorine compounds were present above the limit of detection. The FEP sample had similar concentrations of TFA and PFPrA between NMR and IC-MS, however NMR also indicated the presence of additional long-chain PFCAs including PFPeA, PFHxA, and PFOA. This is suggested by the more complex alkyl-CF_2 region of the NMR spectrum. The presence and concentration of these long-chain PFCAs was confirmed by UHPLC-MS/MS (SI and discussed below), and aligns with observations of PFCAs with carbon chains longer than 4 carbons being observed in other fluoropolymer products.

In addition to fluoropolymer tubing where NMR indicated additional non-targeted organofluorine species in some samples, PEEK tubing was extracted and analyzed by NMR. PEEK tubing was not available for the IC-MS analysis and was only subject to NMR. PEEK tubing is often used as a replacement for fluoropolymer tubing in analytical systems such as UHPLC-MS/MS where trace analysis of PFCAs is desirable, and the presence of fluoropolymer tubing is suspected to lead to additional instrument background. However, NMR results indicate the presence of numerous organofluorine compounds in the PEEK tubing extract including ultra-short

PFCAs and aryl fluorine species. The presence of C_2-C_3 PFCAs in the PEEK extract was confirmed qualitatively by UHPLC-MS/MS. The presence of aryl fluorine atoms could be a result of manufacturing process, which in some cases uses 4,4'-difluorobenzophenone (4,4'-DFB) and 4-fluorobiphenyl as polymerization and end-capping reagents.[36] The NMR results demonstrate the necessity for researchers to use a multitude of techniques. While targeted methods are excellent at providing quantitative information, where compounds are not included in target lists or are not amenable to ionization techniques, there is a potential that additional compounds may be missed.

UHPLC-MS/MS analysis was performed on the same samples that were prepared for ^{19}F NMR analysis. One sample per polymer type was prepared and analyzed given the longer acquisition time on the NMR. Standard deviations reported represent instrumental precision, and are therefore much smaller than IC-MS results where three separate pieces of tubing were examined. UHPLC-MS/MS and NMR reported very similar concentrations of PFBA, within the range of IC-MS analysis (Table S5), suggesting instruments do not cause any artefacts. UHPLC-MS/MS allowed for quantitative analysis of C_4-C_{10} PFCAs (Table S6). The only PFCA from C_5-C_9 to be measured above 2 ng/g was PFOA, which aligns with other observations from fluoropolymers.[28] The highest concentration was in samples PTFE1, PTFE2, and PFA1, all with concentrations from 22-24 ng/g. Although PFA1 had 23.8 ng/g PFOA, PFA2 only had 2.77 ng/g, showing differences between the production of PFA. PEEK, which is not a fluoropolymer, had a concentration of 9.71 ng/g PFOA, which aligns with the need for delay columns in HPLC systems using PEEK tubing, where a delayed peak for PFOA can be observed.[23]

Table 1. Summary of PFAS identified from each polymer type. **bold** typeface represents > 10 ng/g, normal typeface represents ≥ 1 ng/g (below 1 ng/g omitted from table). When more than 1 sample of a polymer type was tested (e.g. PTFE1 and PTFE2) if the analyte was present in one, it is included in the table.

Polymer type	Monomer(s)	Structure	Leachate products identified
PTFE	Tetrafluoroethylene		TFA PFPrA **PFBA** PFHxA **PFOA**
PFA	Tetrafluoroethylene and perfluoroalkyl vinyl ethers (PAVEs): methyl (PMVE), ethyl (PEVE), or propyl (PPVE, drawn)		**TFA** **PFPrA** PFHxA **PFOA**
FEP	Tetrafluoroethylene and hexafluoropropylene		**TFA** PFPrA PFBA PFOA
PVC	Vinyl chloride		TFA PFBA PFOA
PP	Propene		TFA PFPrA
PEEK	Polyether ether ketone		TFA PFBA 4,4'-DFB Unknown aryl-F

4. IMPLICATIONS

This work identifies laboratory polymers as sources of ultra-short chain PFCAs and other PFAS to the environment, from both fluoropolymers and non-fluorinated polymers. Overall, fluoropolymers had higher concentrations of PFAS in their aqueous leachate, and the predominant PFAS depended on polymer type. For trace laboratory analysis of PFAS, these sources of PFCAs, especially the ultra-short chain PFCAs can cause challenges with blank contamination and can impact results of total fluorine or non-targeted approaches if not properly managed. Even PEEK, a common polymer used to avoid PFAS, can leach ultra-short chain PFCAs and other PFAS, although we cannot confirm whether the source was the polymer itself or if it collected the PFAS during production, transport and storage. Our measurements suggest the PFAS community can take steps to prevent polymer contamination in analysis of ultra-short chain PFCAs. From sequential aqueous extraction of the tubing, we observed tubing was effectively cleaned for TFA and PFBA, but not PFPrA, especially not from PFA tubing. More work is needed to understand the behaviour of PFPrA. Finally, we suggest C_{18} trap columns on HPLC systems be re-evaluated to assess their effectiveness for the delay, especially for TFA and PFPrA which are poorly, if at all, retained on most C_{18} stationary phases. Mixed-mode or IC phases as trap columns should be assessed as alternative options.

We observed high heterogeneity between samples of the same polymer type (Figure 1), both in replicates of the same tubing part number and between tubing of the same material but different part numbers (i.e. PFA1 and PFA2, PFTE1 and PTFE2). Manufacturing processes vary, and we were not able to obtain the manufacturing processes for our specific samples. Additionally, we cannot know if the PFAS measured here was a result of the manufacturing process or whether it was a result of sorption from other sources during shipping, handling, and storage. There is evidence that fluoropolymers and non-fluorinated polymers can sorb PFAS.[37,38] Overall, the

preliminary nature of these results highlights the need to better characterize small molecule PFAS originating from all types of polymer materials.

Measured concentrations of TFA, PFPrA and PFBA were often much higher than PFOA and other C_5-C_9 PFCAs from the tubing samples. Previous measurements of PFAS from personal care products containing fluoropolymers should be revisited to determine if these products also contain high levels of TFA and PFPrA, analytes which were not included in the original measurements. High levels of TFA and PFPrA have been observed in landfill leachate,[39] and our results suggest that discarded polymers may be one source contributing to those point source contamination levels.

ASSOCIATED CONTENT

Supporting Information. Details of polymer samples, instrumental analysis, tabulated results, and NMR spectra are included in the Supplementary Information.

The following files are available free of charge.

Supplementary Information (PDF).

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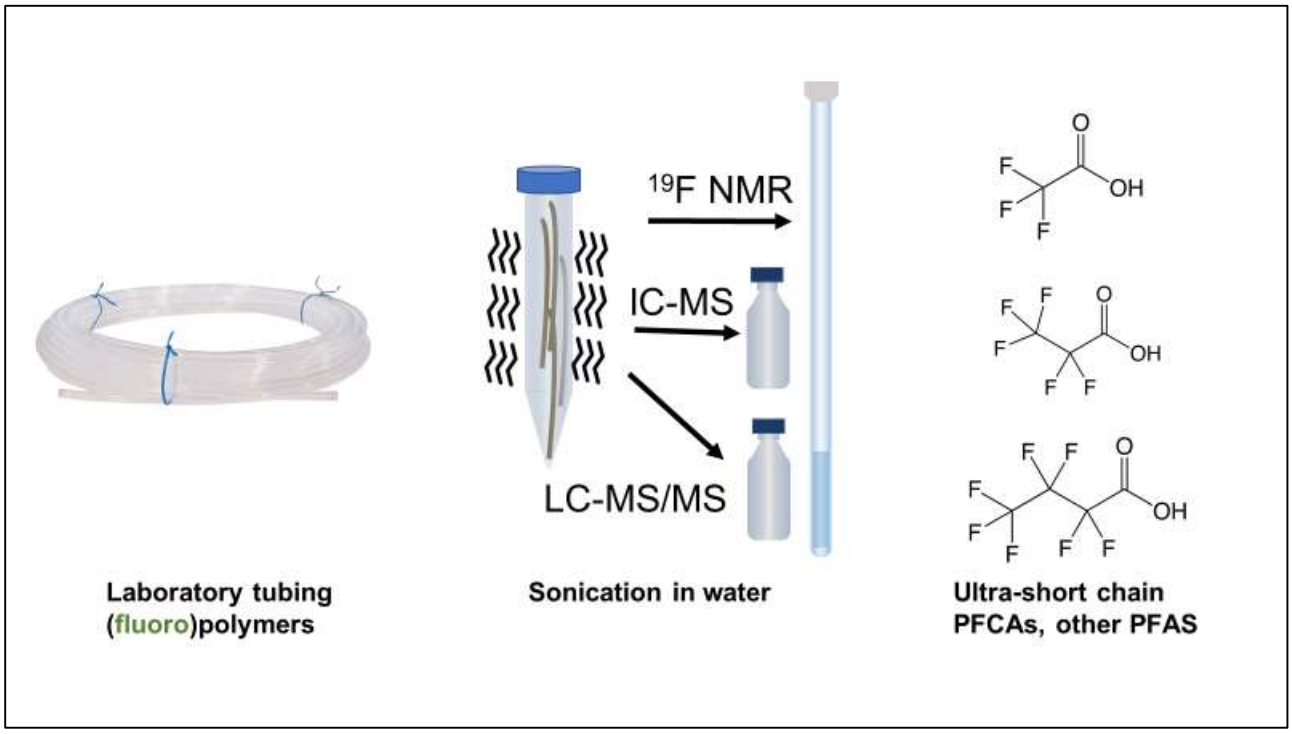
TOC ART


^{19}F NMR
IC-MS
LC-MS/MS
Laboratory tubing
(fluoro)polymers
Sonication in water
Ultra-short chain
PFCAs, other PFAS