

CHARACTERISATION OF TECHNICAL MIXTURES CONTAINING SIDE-CHAIN FLUORINATED POLYMERS

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Introduction:

Per- and polyfluoroalkyl substances (PFASs) are an extensive group of man-made amphiphilic organic compounds¹, that are suspected to pose a risk to the environment due to their persistence, mobility and toxicity. Their unique physicochemical properties such as low surface tension and thermal and chemical stability have resulted in a wide range of industrial and commercial applications. The latest report from OECD identified over 4700 PFAS-related compounds on the global market²; however, only a minor part of them are commonly monitored in environmental samples. Since most of the environmental research focused mainly on non-polymer aliphatic PFASs such as PFCAs, PFASs and some of their potential precursors, knowledge about existence and characteristics of polymeric PFASs is limited³⁻⁵.

Polymeric PFASs have been speculated to be possible precursors to PFSAs and PFCAs⁵. Side-chain fluorinated polymers are compounds with a structure of a non-fluorinated polymer backbone with per-/ polyfluorinated side-chains⁶. Side-chain fluorinated polymers are commonly applied to materials to give oil- and water repellency. A recent investigation studied two Scotchgard products (fabric protector sprays from the trademark Scotchgard™ by the 3M Company) produced before 2002 and after 2002 and concluded that these products contained side-chain fluorinated polymers⁴. The study showed detectable levels of these products in aquatic sediment and biosolid-augmented agricultural soil from North America. Their chemical identities are a tradeseecret of 3M Company and therefore are their structures not yet determined. Perfluorooctanesulfonyl-based (C8) chemistry was used in the pre-2002 formulation and shift to perfluorobutanesulfonyl-based (C4) chemistry in the post-2002, due to the phase-out of C8 chemistry by the 3M Company at 2002⁷.

The purpose of the present study is to understand the fate and transport of these suspected side-chain fluorinated polymers in the environment by studying their structure and characteristics. The objectives were to i) develop analytical methods to extract and quantify the two technical mixtures containing pre- and post-2002 Scotchgard™ products using LC-qTOF and LC-MS/MS, ii) conduct hydrolysis and sorption tests to understand the fate and transport of these products, which could give an insight about their structure and characteristics, and iii) estimate the fluorine content of the Scotchgard™ products using combustion ion chromatography. Further goal is to apply the developed analytical methods to Swedish municipality sludge samples to evaluate if these Scotchgard™ technical mixtures are present in the Swedish environment and could explain the unidentified organofluorine in a previous study.⁸

Materials and Methods:

Technical mixtures of Scotchgard™ pre-2002 formulation (100 µg/mL in methanol) and Scotchgard™ post-2002 formulation (100 µg/mL in methanol) were purchased from AccuStandard Inc. (New Haven, CT, USA). The sediment used for method optimisation and the sorption test was a low PFAS-contaminated sample (>20 cm depth) taken from a freshwater lake.

The extraction methods tested during the present study were ultrasonication with hexane:acetone (1:1), with a disposable silica gel SPE and an extra dispersive SPE clean-up⁴; ion-pair extraction modified from Hansen et al.⁹; and an liquid-liquid extraction with MTBE.

Quantitative analyses of pre and post-2002 formulations using LC-MS/MS were performed according to a previous study¹⁰ with some modifications. The pre- and post-2002 formulations and 7 PFASs (PFOS, PFBS, FOSA, Et-FOSA, Me-FOSA, FBSA, Me-FBSA) were quantified by a Water Acquity Ultra Performance Liquid Chromatograph (UPLC) with a C18 BEH column (2.1 x 100 mm, 1.7 µm) coupled to a Waters XEVO TQ-S tandem mass spectrometer. The mobile phases were 70:30 water: methanol (A) and methanol (B), both with 2mM of ammonium acetate. Further identification, structural investigation and confirmation of components of pre- and post-2002 formulations were done with a Waters Acquity UPLC coupled to a Waters Xevo G2-XS QToF Quadrupole Time-of-Flight Mass Spectrometer. The total fluorine content in the pre- and post-2002 formulations were determined by using a combustion ion chromatograph (CIC) from Metrohm AG.

Hydrolysis experiments were performed on the technical mixtures of pre- and post-2002 with both high and low water contents (90% and 10%). The hydrolysis was performed by mixing a standard solution of either pre- or

post-2002 (2000 ng/mL) with water and methanol at high and low pH (NaOH/HCl). Three different solutions used to accelerate the hydrolysis reaction were tested: 1M NaOH, 0.1M NaOH and 0.1M HCl. The mixtures were kept in a water bath (60°C) for 4 hours and shaken every 20 minutes. The mixtures were allowed to stand for 3 days before being analysed for aliphatic PFASs, and pre- and post2002 by UPLC electrospray ionisation tandem mass spectrometry (UPLC-ESI-MS/MS) in negative mode. The hydrolysis experiments were further studied by direct infusion on Waters Xevo G2-XS qTOF.

In order to quantify the leaching of the technical mixtures of pre- and post-2002 from particles, a sorption test was performed by adding technical mixtures of pre- or post-2002 (1000 ng/mL respectively) to sediment (1, 0.5, 0.1 g) at a liquid to solid ratio of 15. The mixtures were shaken for 24 hours or 7 days after which the aqueous phase was extracted by liquid-liquid extraction using MTBE. An extraction blank was made with each extraction together with three blank sediment samples treated the same way as the spiked samples. The concentration of pre- and post-2002 in the leachate waters were measured by UPLC-TQS MS/MS.

Results and Discussion:

Analyses of technical mixtures. One of the aims of the current study was to develop an analytical method using LC-qTOF, however, several challenges were encountered. Direct MS infusion using qTOF-MS of the technical mixtures did not give any specific information about the fluorinated ingredients in the technical mixtures of pre- and post-2002 used in Scotchgard™ fabric protector (Figure 1A). These mixtures were complex and the MS-spectra were difficult to interpret. Without LC separation, the main component in technical mixtures, as identified from the previous study (pre-2002: m/z 1315.05 and m/z 1634.3 for post-2002), was not observed due to low intensity (Figure 1A). The mass spectra improved with LC separation and displayed product ions and similar fragment profiles for both mixtures as presented in the previous study³, with some small differences (Figure 1B). The differences in fragmentation patterns could be because a different instrument was used in the current study.

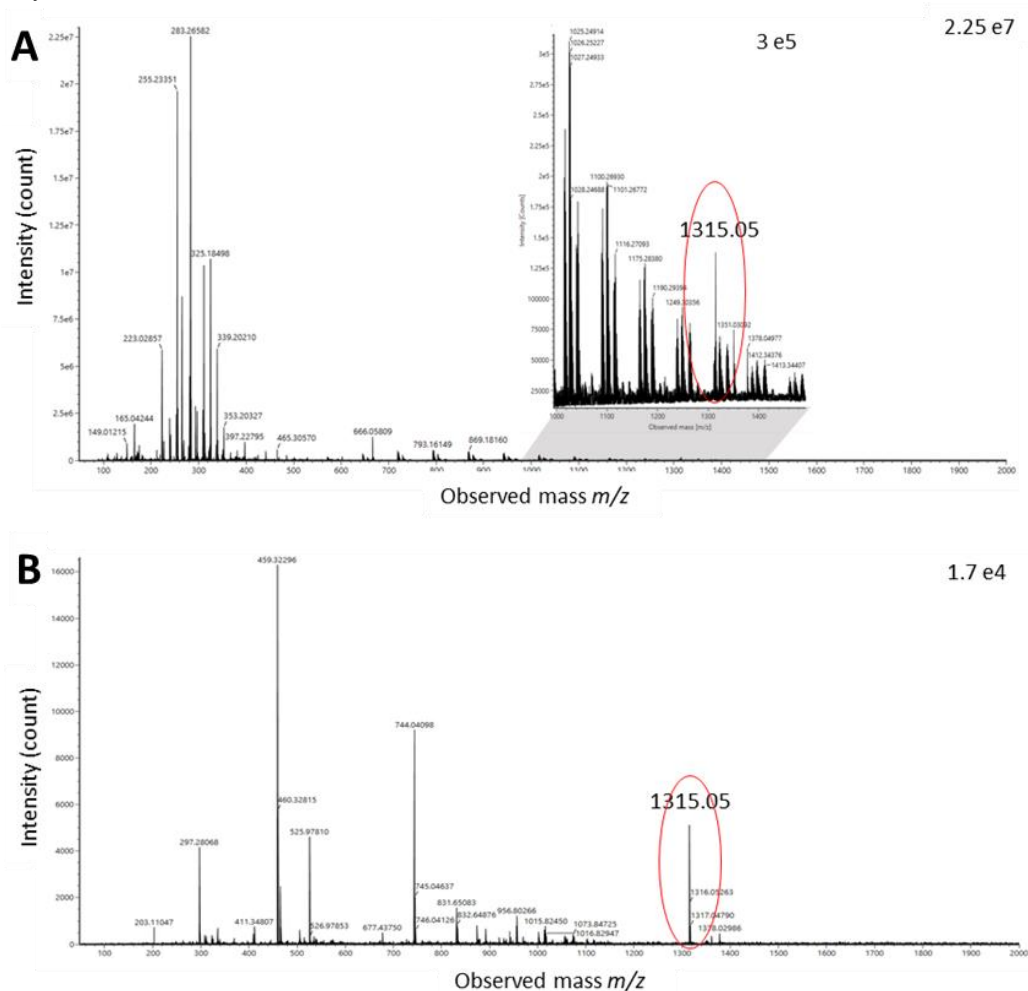


Figure 1. A. Mass spectra of direct MS injection of technical mixture pre-2002 (1000 ng/mL) using UPLC-ESI(-)-qTOF (MS/MS), an enlarged picture of the spectra where the suspected precursor ion is shown. B. Mass spectra of technical mixture pre-2002 (1000 ng/mL) after LC separation.

The MS parameters were optimised with LC separation. Higher capillary voltage gave increased intensity for the precursor ions and was therefore set to 3 kV. Desolvation temperature and source temperature were at 400 °C and 150 °C, respectively. Desolvation and source gas flow were 800 L/h and 150 L/h, respectively.

In the current study, a C18 BEH porous column was used, and broad and fronting peaks were observed for both technical mixtures (Figure 2). The broad peaks could be due to co-elution of interfering substances or the presence of structural isomer.

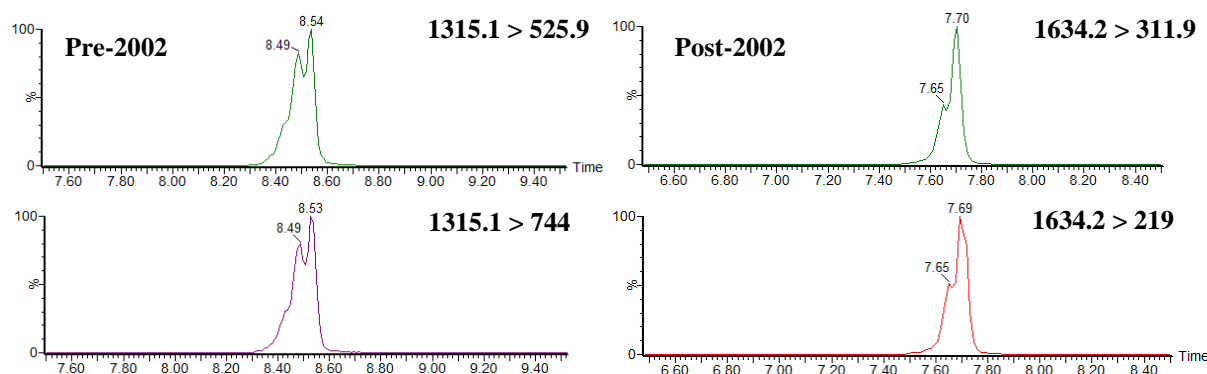


Figure 2. Mass chromatograms showing two different transitions of main components of pre-2002 (left) (1315.1>525.9 and 1315.1>744) and post-2002 (right) (1634.2>311.9 and 1634.2>219) in a standard spiked

Our previous studies showed high presence of unidentified organofluorine (OF) in sludge and sediment samples^{8, 11}, these sample extracts were re-analysed using current settings on the LC-MS/MS, to see if these two compounds could explain a portion of the unidentified OF. However, only one out of nine sample extracts showed detectable peaks, suggesting that these products were not likely to account for the unidentified OF in these extracts. Differences in extraction methods could also be the reason for absence of detectable levels of the technical mixtures of pre- and post-2002 and will be further analysed.

Extraction and clean-up. Three different extraction methods were tested using spiked sediment and two clean-up methods were tested on spiked water. For sediment samples, our results showed that the method using acetone:hexane (1:1) as extraction solution resulted in better recoveries for pre- and post-2002 at 86% and 41%, respectively, compared to the extraction methods with MTBE (57% and 25% recovery, respectively) and ion-pair extraction (35% and 26%, respectively). For water samples, both ion-pair and MTBE extraction could extract both suspected side-chain fluorinated polymers with approximately 100% recovery, which indicated that both of these extraction methods could be used as a clean-up after isolation of the suspected side-chain fluorinated polymers from the sample matrix. We further optimised the composition of extraction solution (different ratios of acetone and hexane) and concluded that the composition of 70:30 acetone:hexane gave the best extraction recoveries for both products. These extraction methods will be applied to Swedish municipality sludge samples to determine their levels.

Characterisation and behavior. Our preliminary results from the hydrolysis experiments showed that only approximately 2-52% of pre and 0-45% of post were hydrolysed; detectable levels of PFBS was found in the post-2002 samples. An interesting thing was that the chromatograms of the samples showed different peak shapes before and after the hydrolysis experiments (Figure 3). The co-elution (the shoulder) as discussed above reduced in the pre-2002 and disappeared in the post-2002 and it may be due to the degradation of the side-chain. Similar patterns were also observed with the different extraction methods as discussed above. Further investigations are needed to clarify this point.

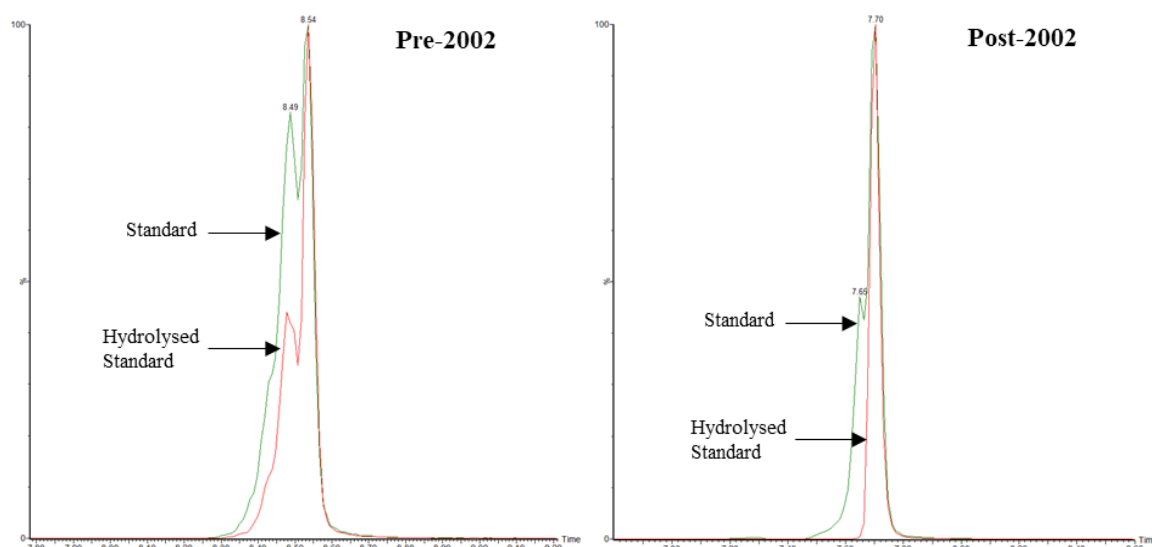


Figure 3. Combined mass chromatograms of main components for pre-2002 (left) in a standard (green) and hydrolysed standard (red) and post-2002 (right) in a standard (green) and hydrolysed standard (red) analysed by UPLC-TQS MS/MS. The standard were spiked at 600 ng/mL.

The results of our sorption experiments showed that these suspected side-chain fluorinated polymers were readily adsorbed onto particles. Minor leaching was seen for the post-2002 in the lowest amount of solid (0.1 g), where 0.48% was detected in the aqueous phase after 24 hours.

Both technical mixtures were analysed for total fluorine content using CIC. The measured technical mixtures (100 µg/mL) showed 596 ± 130 ng F/mL for the pre-2002 and 2040 ± 115 ng F/mL for the post-2002, respectively. The concentration of fluorinated chemicals in Scotchgard™ products for commercial use has been reported to be <3% by weight¹². Given the stated concentration of the technical mixtures (100 µg/mL), the fluorine from the total fluorine measurement accounted for 0.46-0.73% (pre-2002) and 1.9-2.2% (post-2002) of the technical concentration.

Current study showed that these suspected side-chain fluorinated polymers were readily adsorbed to particles and may indicate their fate in the environment. The high percentage of unidentified OF in previously analysed sludge and sediment could not be explained by pre- and post-2002 formulations. Additional studies are necessary to explain further their existence, fate and route in the environment.

Acknowledgements:

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