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Discovery of novel per- and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility

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- 19       • Mass defect filtering strategy allowed the detection of untargeted PFASs  
20       • Novel PFASs homologues were detected in soil and concrete samples collected at the  
21       FTG

22

## 23 **ABSTRACT**

24 Aqueous film forming foams (AFFFs) have been released at fire training facilities for several  
25 decades resulting in the contamination of soil and groundwater by per- and polyfluoroalkyl  
26 substances (PFASs). AFFF compositions are proprietary and may contain a broad range of  
27 PFASs for which the chemical structures and degradation products are not known. In this  
28 study, high resolution quadrupole-time-of-flight tandem mass spectrometry (LC-QTOF-  
29 MS/MS) in combination with a data processing using filtering strategies was applied to  
30 characterize and elucidate the PFASs present in concrete extracts collected at a fire training  
31 ground after the historical use of various AFFF formulations. Twelve different  
32 fluorochemical classes, representing more than 60 chemicals, were detected and identified in  
33 the concrete extracts. Novel PFASs homologues, unmonitored before in environmental  
34 samples such as chlorinated PFASs, ketone PFASs, dichlorinated PFASs and perfluoroalkane  
35 sulphonamides (FASAs) were detected in soil samples collected in the vicinity of the fire  
36 training ground. Their detection in the soil cores (from 0 to 2 meters) give an insight on the  
37 potential mobility of these newly identified PFASs.

38 **Keywords:** Non target analysis, PFASs, contaminated soil, groundwater contamination,  
39 Aqueous Film Forming Foam (AFFF), LC-QTOF-MS/MS.

## 40 **INTRODUCTION**

41 Aqueous film forming foams (AFFFs) have been used since the 1960s for emergency  
42 response and regular training exercises by fire departments at military bases and civil

43 airports. Fluorosurfactants contribute to the performance of the foams by dispensing low  
44 surface tension and by forming a film over the hydrocarbon fuel to prevent re-ignition  
45 (Moody and Field, 2000). Numerous studies have reported the link between the historical use  
46 of AFFFs at fire training facilities and the contamination by fluorosurfactants of the  
47 surrounding environment including biota (Ahrens et al., 2015; Filipovic et al., 2015; Gewurtz  
48 et al., 2014; Kärrman et al., 2011), soil (Ahrens et al., 2015; Filipovic et al., 2015; Houtz et  
49 al., 2013; Kärrman et al., 2011; McGuire et al., 2014), surface water (Ahrens et al., 2015;  
50 Filipovic et al., 2015; Kärrman et al., 2011) and groundwater (Backe et al., 2013; Barzen-  
51 Hanson et al., 2017; Filipovic et al., 2015; Houtz et al., 2013; McGuire et al., 2014; Schultz et  
52 al., 2004). In several cases, the plume of contamination reached well water (Weiß et al.,  
53 2012) and drinking water reservoirs (Gyllenhammar et al., 2015; Jakobsson et al., 2014)  
54 raising public concern of human exposure (Gyllenhammar et al., 2015; Jakobsson et al.,  
55 2014; Weiß et al., 2012) and the potential risks for human health.

56 Fluorosurfactants used in commercially available AFFF formulations vary by year of  
57 production and manufacturer (Place and Field, 2012; Weiner et al., 2013) and the specific  
58 chemical composition is not provided. Comparing total organic fluorine content to the sum  
59 concentrations of known fluorosurfactants have revealed the presence of a significant  
60 proportion of unknown organic fluorine compounds in AFFF formulations either  
61 manufactured by electrochemical fluorination (ECF) or telomerisation (Weiner et al., 2013).  
62 The quantification of 25 targeted PFASs elucidated between 10% and 50% of the total  
63 organic fluorine over the 11 commercially available AFFFs analysed by total organofluorine-  
64 combustion ion (Weiner et al., 2013). Similar observations were made following the analysis  
65 of surface water samples from a creek impacted by an accidental AFFF spill of thousands of  
66 litres (Moody et al., 2002). In this case, the analysis of 12 perfluoroalkyl acids accounted in  
67 some samples for only 13% of the total concentration of PFASs determined by  $^{19}\text{F}$  NMR.

68 These findings underline the presence of a significant amount of other fluorinated chemicals  
69 that have not been identified and for which the fate and environmental impact are not known.

70 Based on different analytical strategies involving high resolution mass spectrometry  
71 (HRMS), several studies have investigated the unknown fraction of fluorosurfactants present  
72 in different AFFFs and provided the identification of new fluorinated homologues and/or  
73 families (D'Agostino and Mabury, 2014; Place and Field, 2012). D'Agostino et al. identified  
74 12 novel PFAS classes based on the analysis of AFFF formulations (D'Agostino and  
75 Mabury, 2014). The strategy employed was based on a combination of the screening of  
76 fractionated AFFF samples using total organofluorine-combustion ion chromatography  
77 followed by HRMS analysis. Place et al. identified 10 novel PFAS classes through 6 different  
78 AFFF formulations using the combination of a pre-screening by fast atom bombardment mass  
79 spectrometry and followed by LC-QTOF-MS/MS (Place and Field, 2012). (Barzen-Hanson et  
80 al., (2017) discovered 40 novel PFASs classes with LC-QTOF-MS/MS through non-target  
81 analysis using Kendrick mass defect plots. Rotander et al. identified several new PFASs with  
82 LC-QTOF-MS/MS based on a metabolomics strategy by comparing the serum of firefighters  
83 exposed to AFFFs to an unexposed population (Rotander et al., 2015).

84 To gain more insight into the fate of PFASs released at firefighter training sites, it is  
85 important to understand the composition of the AFFF formulations applied at the site as well  
86 as the transformation products that can be generated after the release of the foam in the  
87 environment. Indeed, the non-fluorinated section of the PFASs may be subject to microbial or  
88 chemical transformation and generate other hazardous chemicals (Buck et al., 2011). Failure  
89 to identify and monitor all these chemicals could lead to a greater uncertainty on the  
90 environmental impact linked to AFFFs released.

91 For these reasons, the present study aimed to characterize the PFASs present at a fire training  
92 ground (FTG) after the historical use of AFFF formulations. Extracts from concrete samples  
93 collected from the fire training pad have been analysed by LC-QTOF-MS/MS to screen for  
94 newly identified and legacy PFASs and attempt to identify unknown PFAS and/or  
95 degradation products. Following this step, the presence of the PFASs identified in the  
96 concrete extract was then investigated in soil cores (at -0.5, -1, -1.5 and -2 meters) collected  
97 in the vicinity of the fire training pad to get an insight on their potential mobility. As identical  
98 AFFF formulations have been used overtime at different FTG, the contamination profile  
99 observed at the fire training ground assessed in this study, maybe considered to be typical of  
100 other firefighting grounds in Australia.

## 101 **EXPERIMENTAL**

102 **Sample Site.** The FTG is located in Australia and has been an operational fire training  
103 facility since 1988 (Badel et al., 2015b). Until 2010, approximately 3000 L of AFFF  
104 concentrates were used every year. ECF based foam (3M Lightwater) was used from 1988  
105 until 2001 when the transition to telomer-based foam (Ansul) occurred. The transition to  
106 fluorine free foam (Solberg®) followed in 2010. A map of the sampling sites is presented in  
107 supporting information (S1).

108 **Concrete and soil core sampling.** Concrete dust samples ( $\approx 5$  g) were collected using a  
109 drill at 4 different areas of the training pad to ensure adequate representation. Drill bits  
110 were clean with methanol before sample collection. Concrete powder samples were wrapped  
111 in aluminium foil and stored in Ziploc bag at  $-4$  °C. Two soil cores were collected at 20 m  
112 from the FTG and a third core at around 80 m by using a hydraulic drilling rig Geo 305. The  
113 equipment was capable of providing an intact soil core to a depth of 2 m (4 consecutive

114 sections of 50 cm) where the water table was encountered. The soil cores samples were stored  
115 in amber plastic tubes of 50 cm at -4°C until analysis.

116 **Chemicals and Extraction.** Details of extraction procedure employed as well as chemicals  
117 and standards used are available in the supporting information (S2).

118 The soil samples were freeze dried overnight and then sieved through a soil riddle (1.18 mm  
119 mesh size). Concrete dust (0.1 g) or sieved soil (1 g) was weighted and transferred to a falcon  
120 tube (15 mL). Mass labelled-internal standards were added and the samples were then  
121 extracted with MeOH/NH<sub>3</sub>aq (99/1) using ultra-sonication. After centrifugation, the  
122 supernatants were transferred to another falcon tube (15 mL), neutralised with acetic acid and  
123 concentrated to 1 mL under a gentle stream of nitrogen. The samples were then cleaned  
124 through a pre-rinsed ENVI-Carb cartridge (100 mg, Supelclean™ ENVI-Carb™ SPE Tube,  
125 Supelco) and filtered (RC filter 0.2 µm, Phenomenex). After the clean-up, 100 µL of the  
126 concrete extract was collected and transferred directly to Polypropylene (PP) inserts. The  
127 entirety of the soil extract was then transferred and concentrated down to 100 µL in  
128 Polypropylene inserts. Performance standards and 150 µL of 5 mM ammonium acetate in  
129 water were added prior to analysis.

130  
131 **LC/Electrospray Ionization (ESI)-QTOF-MS/MS-Analysis.** Chromatographic separation  
132 of the analytes was carried out using a Shimadzu Nexera X2 ultrahigh-pressure liquid  
133 chromatography (UHPLC) system equipped with a binary pump and a reverse-phase Luna  
134 C<sub>18</sub> column (3 µm x 2 mm x 150 mm, Phenomenex). An extra guard column (C18) was  
135 installed between the solvent reservoirs and the injector to exclude PFASs that originated  
136 from the HPLC system. The UHPLC was coupled to a hybrid quadrupole time-of-flight mass  
137 spectrometer system, Triple-TOF 5600 system (AB Sciex), with an ESI interface working in

138 negative ionization mode. MS was operated in full-scan TOF-MS and MS/MS mode with  
139 information-dependent acquisition (IDA) in a single run analysis (Baduel et al., 2015a);  
140 detailed information can be found in supplementary information (S3).

141 **Data Processing Strategy.** Mass defect is the difference between the compound exact mass  
142 and its nominal mass (Sleno, 2012). Mass defect filtering strategies have previously been  
143 applied through post-acquisition processing of data to remove all signals outside a defined  
144 mass defect range characteristic of the chemicals of interest (Barzen-Hanson et al., 2017;  
145 Barzen-Hanson and Field, 2015; Crimmins et al., 2014; Liu et al., 2015; Myers et al., 2014).  
146 The mass defect range of PFASs is very unique and ranges between 0.85 and 1. In this study,  
147 a selective extraction of the data was performed by filtering out all signals corresponding to  
148 other mass defect values which were not included in the range from 0.85 to 1. This strategy  
149 provided a decrease in the number of ions to elucidate from 3597 to 476 spectra. To further  
150 reduce the number of spectra to investigate the signal intensity was set to be greater than  
151  $2.3 \times 10^3$ . The number of chemicals of interest then decreased to only 172 parent ions and were  
152 then investigated based on the quality and the intensity of the signal. Once a suspect PFAS  
153 parent ion was selected, the ion was first confirmed to not be present in the procedural blank  
154 samples. A manual PFAS homologue search can be performed by searching for m/z spacing  
155 by  $\pm 50$  (i.e.  $-\text{CF}_2$ -) or  $\pm 100$  (i.e.  $-\text{CF}_2\text{-CF}_2$ -) as PFASs are manufactured as chain-length  
156 homologues when manufactured by ECF or telomerisation respectively (Liu et al., 2015). The  
157 confirmation of non-target analytes and structural characterization of unknown analytes was  
158 performed using PeakView software (AB Sciex) including the Formula Finder tool.  
159 Compound identification was based on the accurate mass measurement (mass error  $< 5$  ppm),  
160 elemental composition assignment, isotopic pattern distribution, ring and double bonds  
161 (RDB) factor and MS/MS spectrum interpretation. A general elemental composition limit  
162 was set (i.e. carbon: 0-40; hydrogen: 0-40; fluorine: 0-60; oxygen: 0-10; nitrogen: 0-2;



163 sulphur: 0-2; phosphorous: 0-2) but was adjusted when justified by characteristic isotopic  
164 patterns (presence of Chlorine and Bromine) or the presence of well-known fragments.

165 **Quantification and Quality Assurance.** Procedural blanks and instrumental blanks were  
166 analysed along with each sample injection to check for cross contamination, analytes  
167 carryover and background response. Three replicates of soil samples and two replicates of  
168 concrete samples were performed to control the reproducibility of the method for the  
169 detection of untargeted compounds. The method reporting limits for the targeted PFSA and  
170 PFCAs in this study were between 0.2 and 1.3  $\mu\text{g}\cdot\text{Kg}^{-1}\cdot\text{d.w.}$  and are provided as well as the  
171 method validation parameters in the supporting information S4. Calibration standards were  
172 made up in 250  $\mu\text{L}$  (150  $\mu\text{L}$  methanol/100  $\mu\text{L}$  5mM ammonium acetate in water) in the range  
173 between 0.1 and 100  $\text{ng}\cdot\text{mL}^{-1}$  (0, 0.1; 0.2; 1; 4; 10; 20; 40; 100). Quantification was  
174 performed for PFCAs (C4 to C12) and PFSA (C4, C6, C8 and C10) and 6:2FTS using  
175 corresponding reference standards available in the laboratory and all values reported were  
176 corrected for recovery of the corresponding surrogate standards (S5). For the other analytes,  
177 where no analytical standards were available, semi-quantification was performed using the  
178 response factor obtained by the PFSA or PFCAs homologue presenting the closest structural  
179 similarity (functional group and/or fluoride carbon chain length, S5).

## 180 **RESULTS AND DISCUSSION.**

181 **Characterisation of PFASs present at the FTG and identification of novel chemicals and**  
182 **homologues.** The filtering strategy applied allowed the identification of several PFASs  
183 families and their isomers in the concrete samples. Mass accuracy was  $< \pm 5$  ppm in full scan  
184 acquisition and isotope score values were higher than 80 % in all cases. The mass accuracy of  
185 the fragments was in most cases  $< 20$  ppm. To provide insights into the fragmentation  
186 mechanisms, a proposed structure for each family was proposed based on the experimental

187 MS/MS spectrum. Supplementary material S6 summarizes the main characteristics obtained  
188 for one homologue of each identified family including MS and MS/MS information. Table 1  
189 reports all PFASs detected and tentatively identified in the concrete extract along with their  
190 MS information, mass error, isotopic fit, retention time. All chemicals reported were not  
191 detected in the procedural blanks. The PFAS families often represent series of homologues  
192 compounds of the same class but with various chain length differing by  $-\text{CF}_2-$  so the  
193 homologues present mass spectral peaks differing by 49.99681 Da. The mass spectrum from  
194 the IUPAC mass scale can be converted to the Kendrick mass scale i.e. multiplying each  
195 mass by  $(50.0000/49.99681)$ .  $\text{CF}_2$  normalized Kendrick mass defect (KMD) was plotted for  
196 all the ions remaining after the filtering strategy (Figure 1). Homologous series presenting an  
197 identical Kendrick mass defect line up horizontally on the Kendrick mass defect plot  
198 confirming that they belong to the same class.

199 **1. Perfluoroalkyl carboxylates (PFCAs).** Targeted PFCA chemicals ( $\text{C}_4\text{-C}_{12}$ ) were  
200 detected and confirmed by matching MS/MS spectra and retention time with analytical  
201 standards. PFCAs have been reported as primary components in early 3M AFFFs from  
202 1965 up to 1975 (Backe et al., 2013; Place and Field, 2012; Prevedouros et al., 2006).  
203 PFCAs can be present as impurities and generated from abiotic and biotic degradation  
204 of fluorosurfactants present in POSF-based and fluorotelomer-based AFFFs (Houtz and  
205 Sedlak, 2012; Prevedouros et al., 2006). The manual search of homologues in the MS  
206 spectra also revealed the presence of perfluoropropanoic acid (PFCA-C3). A low mass  
207 error between theoretical and observed masses (0.9 ppm) was observed as well as a  
208 good isotopic fit (95%). The MS/MS experiment confirmed the structure with  
209 characteristic fragments of PFC ( $68.9957 \text{ CF}_3$ ;  $74.9886 \text{ C}_2\text{O}_2\text{F}$ ). To our knowledge this  
210 is the first time that this short chain PFCA has been tentatively identified at a site  
211 impacted by AFFFs.

- 212 **2. Perfluoroalkyl sulphonates (PFSA).** PFBS, PFH<sub>x</sub>S, PFOS and PFDS were targeted  
213 and detected in all the concrete extracts. Manual searching of the homologues for 50 m/z  
214 spaced ions show the presence of the homologues with a carbon backbone from C<sub>1</sub> to  
215 C<sub>12</sub>. The presence of PFSA homologues was confirmed by the presence of fragments  
216 characteristics of PFSA (e.g., m/z 79.9568, 98.9552, and [M-H]<sup>-</sup>), the low error mass  
217 between observed and theoretical exact masses (i.e. 0.1 ppm to 5 ppm), and an excellent  
218 isotopic fit (94-99%). The MS information for individual homologues is given in table  
219 1. PFSA have been components of 3M AFFF from the 1970s to 2001; PFSA C<sub>6</sub>-C<sub>8</sub>  
220 homologues being the predominant PFSA homologues in AFFFs from 1988-2001  
221 (Backe et al., 2013). Shorter chains C<sub>2</sub>-C<sub>3</sub> PFSA were recently identified in 3M AFFFs  
222 from 1988-2001 (Barzen-Hanson and Field, 2015) and our study present for the first  
223 time to our knowledge the tentative identification of a C<sub>1</sub> homologue.
- 224 **3. Chlorinated perfluoroalkyl sulphonate (PFSA-Cl).** The application of the mass  
225 defect filtering strategy allowed the detection a chemical with m/z of 514.9007. The  
226 isotopic distribution in the full scan mass spectra suggests the presence of one chlorine  
227 atom in the structure (ratio [M-H]<sup>-</sup>; [M-H]<sup>-</sup>+2= ratio of peak height 3/1). The structure  
228 was elucidated by the presence of fragments common to PFSA (e.g., m/z 79.9568,  
229 98.9552, 118.9920) and by the presence of chlorine (m/z 34.9688). The research of  
230 homologues reveals the presence of PFH<sub>x</sub>S-Cl. These two chemicals have been recently  
231 discovered for the first time in serum samples from firefighters exposed to AFFFs after  
232 several decades of duty in Australia (Rotander et al., 2015).
- 233 **4. Discovery of Dichlorinated perfluoroalkyl sulphonate (PFSA-Cl<sub>2</sub>).** The application  
234 of the filter strategy allowed the identification of a chemical with m/z of 530.8711. The  
235 isotopic distribution in the full-scan mass spectra suggests the presence of two chlorine

236 atoms in the structure (ratio  $[M-H]^-$ ;  $[M-H]^{-+2}$ ;  $[M-H]^{-+4}$  = ratio of peak height 9/6/1).  
237 The structure presents fragments common to PFOS (e.g.,  $m/z$  79.9595, 98.9555,  
238 129.9561, 229.9453) and the fragment characteristic of the presence of chlorine ( $m/z$   
239 34.9777). The fragmentation pattern suggests that one Cl atom is in 4<sup>th</sup> position due to  
240 the fragment ( $C_4F_7O_3SCl^-$ , 9.8 ppm). However, fragment information was not sufficient  
241 to identify the 2<sup>nd</sup> chlorine atom position. Moreover, it is possible that this is a mixture  
242 of isomers where the Cl atom can be fixed at different position. To our knowledge this  
243 is the first time that this chemical has been identified. The chemical  $C_3F_5Cl_2SO_3$  was the  
244 only homologue of this family tentatively identified previously in environmental  
245 samples (Crimmins et al., 2014).

246 **5. Discovery of Perfluoroalkene sulphonate (PFSA-unsaturated).** The application of  
247 the filtering strategy allowed the identification of a chemical with  $m/z$  of 460.9334. The  
248 structure was elucidated by the presence of fragments common to PFSAAs (e.g.,  $m/z$   
249 79.9595, 98.9568, 118.996, 168.9888), which was included in the molecular formula  
250 generator. The proposed formula presenting the best fit was  $C_8F_{15}SO_3^-$  (mass error -1  
251 ppm) with one unsaturated site. The mass is similar to the  
252 perfluoroethylcyclohexanesulfonate (PFECHS) (De Silva et al., 2011) an erosion  
253 inhibitor in aircraft hydraulic fluids, but the fragmentation differ by the presence of the  
254 fragments 129.9536 ( $CF_2SO_3^-$ ) and 229,9472 ( $C_3F_6SO_3^-$ ). These fragments suggest that  
255 an unsaturated site might be present from the 4<sup>th</sup> carbon indicating a double bond (rather  
256 than a cyclic structure). The fragments 168.9888 ( $C_3F_7^-$ ), 230.9856 ( $C_5F_9^-$ ) and 280.9749  
257 ( $C_6F_{11}^-$ ) could suggest the presence of a double bond between the 4<sup>th</sup> and 5<sup>th</sup> carbon. The  
258 proposed chemical structure was drawn and compared to the experimental MS/MS  
259 spectrum and is presented in S6. It is possible that there is a mixture of isomers where  
260 the unsaturated site could be a cycle or double bond located at different positions.

261 **6. Discovery of Ketone perfluoroalkyl sulphonate homologues (PFSAs-Ketone).** A  
262 chemical of high intensity was noted with  $m/z$  of 476.9283. The structure was  
263 elucidated by the presence of common fragments (e.g.,  $m/z$  79.9568, 98.9552) which  
264 was included in the molecular formula generator; the proposed formula presenting the  
265 best fit was  $C_8F_{15}SO_4^-$  (mass error -1 ppm) with one unsaturated site. Manual searching  
266 of the homologues showed the existence of 10 homologues spacing by 50  $m/z$ . One with  
267 the lowest molecular mass ( $m/z$  326.9379) was chosen for structure identification. The  
268 absence of fragment of terminal perfluorinated carbon chains such as  $-CF_3$  or  $-C_2F_5$   
269 suggests that the carbonyl might be present at the end of the chain. PFOS with a  
270 carbonyl group has been found previously in firefighter's serum (Rotander et al., 2015).  
271 However, this study found a total of 10 homologues in the concrete extract with the C8  
272 homologue showing the highest signal. The proposed chemical structure was drawn and  
273 linked to the experimental MS/MS spectrum and is presented in S6.

274 **7. Discovery of Perfluoroalkane sulphonamides homologues (FASAs).** PFOSA was  
275 detected in the concrete extracts. The structure confirmation of PFOSA was based on  
276 the presence of the fragments ( $NSO_2^-$ ) e.g.  $m/z$ : 77.9649 and  $[M-H]^-$ , the good isotopic  
277 fit (98.9%) and the low error between theoretical and observed mass (-1.4 ppm). Manual  
278 searching of the homologues for 50  $m/z$  spaced ions show the presence of the  
279 homologues from C3 to C10, the presence of the fragments ( $NSO_2^-$ ) e.g.  $m/z$ : 77.9649  
280 and  $[M-H]^-$  were common to all homologues. The presence of various fragments  
281 (68.9952, 118.9920, 168.9888  $m/z$ ) corresponding to fluorinated chain parts could be  
282 seen for the different homologues at relatively low abundance (<10%). Except for  
283 FASA-C8 and -C6, this is the first time to our knowledge that these homologues have  
284 been identified in AFFF impacted sites. The presence of isomers and homologues

285 spacing with  $-\text{CF}_2-$  indicates that the chemicals are linked to the use of ECF-based  
286 foams.

287 **8. Perfluoroalkyl sulfinic acids (PFSiAs).** The application of the mass defect filter as  
288 well as the filter of intensity allowed the identification of a compound mass at 382.9417  
289 m/z. Taking into account the presence of the fragment 118.9920 ( $\text{C}_2\text{F}_5^-$ ) and 168.9888  
290 ( $\text{C}_3\text{F}_7^-$ ) which was included in the molecular formula generator, the proposed formula  
291 presenting the best fit was  $\text{C}_6\text{HF}_{13}\text{SO}_2$  (error -1 ppm). The proposed structure was drawn  
292 and linked with the experimental MS/MS spectrum (S6). PFSiA-C6 was then tentatively  
293 identified based on the presence of the fragment of  $\text{SO}_2\text{F}^-$  (82.9603 m/z) and the  
294 different fluorinated carbon chains lengths. Spectral investigation for homologues  
295 revealed the existence of C3 to C10 chain lengths chemicals. The fragments  $\text{SO}_2\text{F}^-$  and  
296  $\text{C}_2\text{F}_5^-$  were common to all the homologues. Perfluoroalkane sulfinic acids,  $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{H}$   
297 are degradation products from commercial precursor compounds containing the  
298  $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{N}<$  moiety and could be degradation products of fluorosurfactants from 3M  
299 foam [19].

300 **9. Perfluoroalkyl sulfonamidoethanols, (FASEs).** FASEs homologues were identified  
301 and the homologues presented common fragmentation patterns with the two more  
302 abundant fragments  $\text{SO}_2\text{H}^-$  (64.9697 m/z) and  $\text{CH}_2\text{NO}_2\text{S}^-$  (91.9806 m/z). The chemical  
303 structure of perfluorooctane sulfonamidoethanol was drawn and linked to the  
304 experimental MS/MS spectrum and is presented in S6. For all the homologues, the mass  
305 errors between theoretical and observed masses were low (0-2.7 ppm) and the isotopic  
306 fit satisfactory varying between 75-99%.

307 **10. Fluorotelomer sulfonic acids, (n:2FTSs).** The primary degradation products of the  
308 fluorotelomer-based AFFF foam (including Ansulite) were reported to be the 6:2 and  
309 8:2 fluorotelomer sulfonate and have been found in environmental media around  
310 military bases and FTG sites (Fang et al., 2015; Schultz et al., 2004). 6:2FTS was  
311 detected and quantified using analytical standard. The MS spectra were interrogated to  
312 look for 8:2FTS and homologues for 100 m/z spaced ions.

313 **11. Recently identified PFASs.** A suspect screening was performed to detect the presence  
314 of newly identified PFASs in Ansulite and 3M light water in previous work (Backe et  
315 al., 2013; D'Agostino and Mabury, 2014; Place and Field, 2012). Perfluoroalkyl  
316 sulfonamide amines (n=6 and 8) as well as Fluorotelomer thioamido sulfonates (n=6)  
317 were detected and confirmed by matching the fragmentation patterns with other studies  
318 (S6 and table 1). No perfluoroalkyl sulfonamide amino carboxylates were detected  
319 while these chemicals are known to be components in some 3M formulations (Backe et  
320 al., 2013; D'Agostino and Mabury, 2014).

321 **12. Limitation.** It is important to underline that all the compounds have been tentatively  
322 identified and only the analysis of reference standards will confirm unequivocally the  
323 structures proposed. The present screening allowed the detection of a broad range of  
324 PFASs. However, this screening is not exhaustive as some PFASs may not ionize under  
325 current conditions (cationic PFASs, telomere alcohols, zwitterionic compounds etc.)  
326 (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014).

## 327 **IMPLICATION TO THE SURROUNDING ENVIRONMENT.**

328 All chemicals identified in the concrete samples were then investigated in the soil core  
329 samples collected near the FTG. To understand the vertical profile of the contamination, the



330 collected soil core was subsequently sampled and analysed at 4 different depths: 0.5, 1, 1.5  
331 and 2 meters where the water table sits. Semi-quantitative estimation of non-target and  
332 unknown PFASs concentrations was assessed based on the response factors of the  
333 perfluorinated standards available in the laboratory. The standards assigned for individual  
334 analytes is presented in supporting information (S5). Over the analytes targeted, 42 were  
335 detected and quantified in the soil core samples. The average concentration and the vertical  
336 distribution of the analytes detected in the two cores locating near the FTG are presented in  
337 the figure 2 and in the supplementary material (S7) discussed below. A third core has been  
338 sampled at around 80 m to give an insight on the contamination extend and the results are  
339 shown in supplementary material (S8). From previous studies, it has been shown that the  
340 sorption of PFASs is influenced by the soil composition such as the soil organic carbon  
341 content, the pH, the inorganic fractions and the presence of surfactants (Higgins and Luthy,  
342 2006; Tang et al., 2010; Zhao et al., 2014). The soil composition of the different core sleeves  
343 including the total organic carbon (TOC) percentage and the ratio Si/Al is provided in S9.  
344 PFASs structural characteristics, such as the hydrophilic head group and the chain length are  
345 important factors influencing the adsorption on soil and sediments (typically adsorption will  
346 increase with the chain length). However, FTG areas are complex because training exercises  
347 led also to the release of fuels, solvents and hydrocarbon surfactants. All these chemicals are  
348 expected to affect the transport of PFASs in soil surrounding the FTG and to the best of our  
349 knowledge the behavior of multiple PFASs in the presence of this co-contaminants is poorly  
350 documented (Guelfo and Higgins, 2013).

351 Among PFSAs, homologues with 1 to 11 carbons were found at the site. PFOS was present at  
352 higher concentration than any other PFASs targeted reaching up to 4000  $\mu\text{g}/\text{kg}$  at -0.5 m and  
353 followed by PFHxS and PFHpS among PFSAs. The presence of PFSAs is due to the historic  
354 use of 3M formulation at the studied site. In the 3M formulation from 1989 to 2001 tested,



355 homologues from C2 to C10 are components and their individual proportion relative to PFOS  
356 are in descending order PFHxS(~11%), PFBS(~3%), PFPrS(~2.5%), PFHpS(~2%),  
357 PFPeS(~1%), PFNS(~0.6%), PFDS(~0.5%) and PFEtS(~0.2%) (Backe et al., 2013; Barzen-  
358 Hanson and Field, 2015). The ratios between the different homologues observed in the soil  
359 core are not in accordance with the ratio observed in the different formulations from this  
360 period. Such difference could be due to the past use of a formulation prior to 1989 on the site  
361 constituted by different homologues proportions, and/or the transformation of precursor  
362 overtime of specific PFSAs and/or the different partitioning properties of each chemical to  
363 soil and sediments. The concentration of the small chains homologues (C1-C6) increase with  
364 depth suggesting that these chemicals have been transported downward and have reached the  
365 water table. Hydrophilicity of PFSA increases while the carbon chain length decreases, which  
366 facilitate the transport of the shorter chains through the soil and to the groundwater.  
367 Quantification of short ( $<C_7$ ) and ultra-short chains ( $C_2-C_3$ ) were observed in groundwater  
368 contaminant plume at site where 3M AFFFs were released (Barzen-Hanson and Field, 2015).  
369 Concentrations of PFCAs were significantly lower than PFSAs. Among PFCAs, PFOA and  
370 PFHxA predominate with values reaching up to 40  $\mu\text{g}/\text{kg}$ . The vertical distribution of PFCA  
371 homologues along the core show that homologues with 8 carbons present a higher affinity for  
372 soil and sediments while the shorter chains ( $<C_8$ ) are more mobile along the soil core and  
373 may reach the water table overtime (Fig 2.) which is in accordance to previous studies  
374 (Filipovic et al., 2015).

375 FASAs were present at an important ratio relative to PFSAs. Among FASAs, the homologues  
376 with a chain length from C3 to C8 were detected. FASA-C6 was the FASA homologues  
377 estimated at the highest concentration at each depth (concentration reaching up to 89  $\text{ug}.\text{kg}^{-1}$   
378 d. w.). While FASA-C6 and FASA-C8 have already been detected previously in AFFF  
379 impacted sites, this is the first time that the other homologues have been detected in

380 environmental samples (Backe et al., 2013; D'Agostino and Mabury, 2014; Houtz et al.,  
381 2013; Place and Field, 2012). FASAs were not detected in 3M and Ansulite foam  
382 formulations in previous studies suggesting that these chemicals may be generated after the  
383 release (Backe et al., 2013). Perfluoroalkyl sulfonamide amino carboxylates (PFSaAmA) and  
384 Perfluoro sulfonamido amines (PFSaAm) homologues (C4-C8) are components of 3M foam  
385 (since 1993 to 2001) and these sulfonamide-based chemicals could possibly degrade to  
386 FASAs. The analysis of formulations showed that besides PFOS, PFSaAm-C6 and  
387 PFSaAmA-C6 were the more abundant fluorinated components presenting a ratio relative to  
388 PFOS of 9 and 11 % respectively and a concentration equivalent to PFHxS (Backe et al.,  
389 2013). In this study, PFSaAm -C6 and -C8 are semi-quantified in the soil at low  
390 concentrations ( $<10 \text{ ng.kg}^{-1}$ ) and significantly lower than PFHxS, while PFSaAmA-C6 was  
391 not detected at all. Very low detection frequencies of PFSAm and PFSaAmA homologues  
392 were observed in groundwater at AFFF impacted sites where AFFF formulations (including  
393 3M) were discharged (Backe et al., 2013). Those observations are in accordance with the fact  
394 that they may degrade shortly after release and that FASAs could be potential degradation  
395 products. The concentration of FASAs homologues found in the soil cores and the fact that  
396 these chemicals have been detected through the whole core suggest that they will likely be  
397 detectable in groundwater. Relatively few studies are available on chemicals that belong to  
398 the FASA class. FASA-C8 (PFOSA) was mainly investigated revealing its stability,  
399 bioaccumulation properties and its sorption behavior (Ahrens et al., 2011; Houde et al.,  
400 2011).

401 PFSAs-ketone and chlorinated PFSAs were detected in the soil cores and this is the first time  
402 that those chemicals have been detected in environmental samples. These chemicals may  
403 have been ingredients or impurities in AFFF formulations, or they may be transformation  
404 products generated after release of the foam. PFSAs-Cl presented a maximum concentration

405 of 28  $\mu\text{g}\cdot\text{kg}^{-1}$  d. w. Chlorinated and dichlorinated PFSA concentration decreases along the  
406 soil core and may have a good affinity to soil and organic matter due to the structural  
407 similarity to PFOS. Among Ketone PFSA the homologues C6 to C11 were detected and the  
408 homologue C8 was the most abundant compounds based on the estimates. The shorter chains  
409 show a more rapid migration through the soil suggesting more hydrophilic properties than  
410 PFSA for equal chain length and then a risk to reach and contaminate groundwater.  
411 Bioaccumulative properties of PFOS-Cl and PFOS-ketone have been recently suspected by  
412 their detection in firefighters serum who had been exposed to AFFF foam a decade before  
413 their blood test (Rotander et al., 2015).

414 Fluorotelomer thiamido sulfonates (FTSAS) have been identified as the primary component  
415 of Ansulite formulation (Place and Field, 2012). In the formulation from 2005, 6:2FTSAS is  
416 dominant in Ansulite followed by 8:2FTSAS (18%) and 4:2FTSAS only (0.4%) while no  
417 FTSs was detected in the formulation (Backe et al., 2013; Place and Field, 2012). 6:2FTSAS  
418 was detected at low concentration at the surface of the soil while 4:2FTSAS and 8:2FTSAS  
419 were detected neither in the concrete extracts nor in the soil core samples. On the other hand,  
420 6:2FTS and 8:2FTS were detected in concentration through the core ranging from 1.6-3.4  
421  $\mu\text{g}/\text{Kg}$  and 1.3 to 26.3  $\mu\text{g}/\text{Kg}$  respectively. These findings suggest that the components  
422 8:2FtTAoS and 6:2FtTAoS may have degraded over time and have generated 6:2FTS and  
423 8:2FTS following the dealkylation of the thioether and oxidation of thio group. Indeed,  
424 biotransformation of fluorotelomers from AFFF has been observed in a soil microcosm where  
425 n:2FTSAS was converted to n:2FTS, and n:2FTS was further transformed to the  $C_n$  and  $C_{n-1}$   
426 perfluorinated carboxylates, (Harding-Marjanovic et al., 2015; Weiner et al., 2013) the major  
427 stable degradation products. Other studies identified that 6:2FTS biotransformed relatively  
428 quickly (half-life of 5 days) in aerobic sediment (Zhang et al., 2016), soil microcosm  
429 (Harding-Marjanovic et al., 2015) and slowly in activated sludge (Wang et al., 2011; Weiner

430 et al., 2013) and generated PFPeA, PFHxA as well as polyfluoroalkyl carboxylic acid. On the  
431 other hand no biotransformation was observed in anaerobic conditions so the degradation  
432 may be slow in subsurface environments (Zhang et al., 2016). The concentration of 6:2FTS  
433 was lower than the estimate concentration of 8:2FTS in the soil core and the vertical profile  
434 of 6:2FTS shows a distribution more homogeneous over the whole core than for 8:2FTS  
435 which settles mainly at the surface. While the last application of telomer-based AFFF was  
436 informed to be in 2010, we can then observe relatively slow rates of transformation of  
437 n:2FTS in the environment which could be due to sorption process. However, the  
438 transformation of these different species may serve as a source of additional perfluorinated  
439 carboxylates overtime.

440 In this study we have detected the presence of 42 PFASs in the soil in the vicinity of a fire  
441 training ground. The vertical profile of the soil core showed that a significant amount of  
442 PFASs reached the bottom part of the core, suggesting their potential ability to be transported  
443 and to reach underneath water reservoirs. In Australia there are at least 26 AFFF training sites  
444 for civil aviation and several other for military and other purposes. Sites currently or  
445 historically impacted by the use of PFASs-containing AFFFs have shown a contamination of  
446 the surrounding environment and in some cases drinking water reservoirs. The discovery of  
447 the presence of homologues of FASAs, chlorinated and dichlorinated PFASs and the ketone  
448 PFASs in AFFFs impacted soil at high detection frequency is an important finding. Until  
449 now, those chemicals have gone unmonitored at sites where AFFFs formulations have been  
450 used. The environmental health effects and physico-chemical properties of FASAs,  
451 chlorinated and ketone PFASs are currently not known. The monitoring of these chemicals  
452 would be an asset to determine a more comprehensive risk assessment of AFFF impacted  
453 sites.

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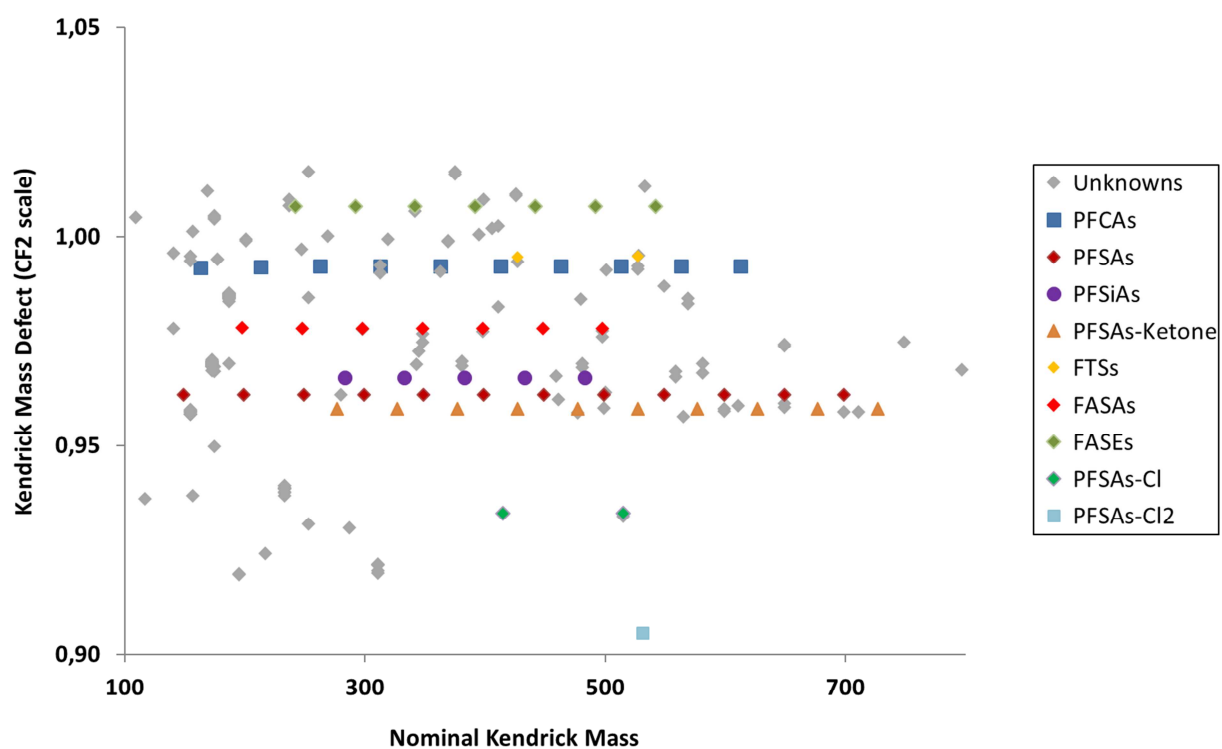
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592

593 **Figure 1.** Kendrick mass defect as a function of nominal Kendrick mass using a mass scale  
594 based on CF2 for ions detected from the concrete extract by the LC-QTOF-MS/MS.

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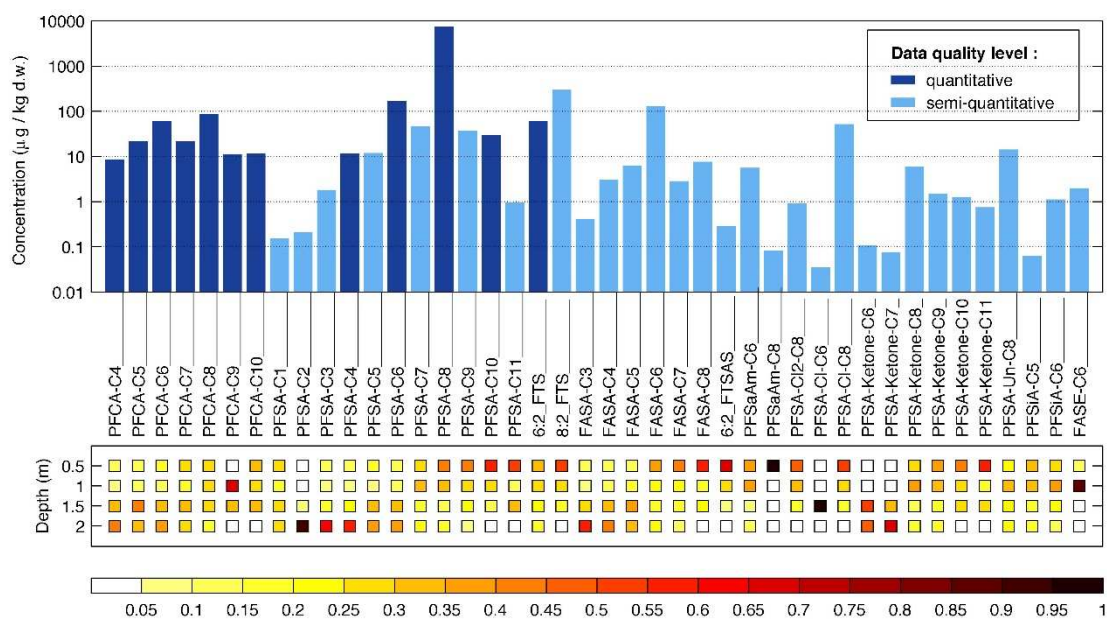


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598 **Figure 2:** Total mean concentration ( $\mu\text{g}/\text{Kg}$  d.w.) and vertical distribution of the PFASs  
 599 detected at 4 different depths (-0.5, -1, -1.5 and -2 meters) in two soil cores. The vertical  
 600 distribution is expressed as a fraction, obtained by dividing the concentration at a specific  
 601 depth by the sum of concentrations obtained over the 4 depths. The mean concentration found  
 602 at each specific depth can be assessed by multiplying the total concentration from the  
 603 histogram by the fraction number corresponding to each specific depth.



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605

606 - **Table 1:** Target, non-target and unknown compounds identified in concrete extract from AFFF impacted FTG using LC-QTOF-MS/MS.

Name and proposed structure	Labels	n	Theoretical mass	Formula	Mass error (ppm)	Isotope Matching (%)	Retention Time (min)		
Perfluoroalkyl Carboxylate $C_n F_{n+1} CO_2^-$	PFCAs	3	162.9823	C3F5O2-	0.9	95	2.36		
		4	212.9792	C4F7O2-	-0.8	99	5.64		
		5	262.9760	C5F9O2-	-1.0	99	9.59		
		6	312.9728	C6F11O2-	-0.9	99	11.76 and 12.11 (L)		
		7	362.9696	C7F13O2-	-0.5	99	13.52 and 13.87 (L)		
		8	412.9664	C8F15O2-	-1.8	99	14.88 and 15.22 (L)		
		9	462.9632	C9F17O2-	-1.7	92	16.32		
		10	512.9600	C10F19O2-	-0.8	98	17.26		
		11	562.9568	C11F21O2-	-2.7	94	18.05		
		12	612.9536	C12F23O2-	-0.7	95	18.75		
		Perfluoroalkyl Sulphonate $C_n F_{2n+1} SO_3^-$	PFSAs	1	148.9526	CF3SO3-	0.2	94	1.48
				2	198.9494	C2F5SO3-	0.9	98	3.26
3	248.9461			C3F7SO3-	-0.1	98	6.80 and 7.05 (L)		
4	298.9429			C4F9SO3-	0.2	98	10.0 and 10.24 (L)		
5	348.9398			C5F11SO3-	-0.9	98	12.01 and 12.40 (L)		
6	398.9366			C6F13SO3-	-3	98	13.68 and 13.99 (L)		
7	448.9334			C7F15SO3-	-2.1	96	14.57 and 14.92 and 15.27 (L)		
8	498.9302			C8F17SO3-	-2.4	98	15.65 and 16.00 and 16.33 (L)		
9	548.9270			C9F19SO3-	-2.5	98	16.55, 16.89, 16.98, 17.23		
10	598.9238			C10F21SO3-	-3.2	98	17.5-18.0		
11	648.9206			C11F23SO3-	-2.1	97	17.90-18.50		
12	698.9174			C12F25SO3-	-1.9	97	18.60-19.0		
Chlorinated Perfluoroalkyl Sulphonate $C_n F_{2n} Cl SO_3^-$	PFSAs-Cl	6	414.9070	C6F12ClSO3-	-0.6	90	13.98 and 14.22		
		8	514.9007	C8F16ClSO3-	-2.5	92	16.21 and 16.50		
Chlorinated Perfluoroalkyl	PFSAs-Cl <sub>2</sub>	8	530.8711	C8F15Cl <sub>2</sub> SO3-	-1.2	61	16.22 and 16.54		

<b>Sulphonate</b> $C_n F_{2n-1} Cl_2 SO_3^-$							
<b>Perfluoroalkene Sulphonate</b> $C_n F_{2n-1} SO_3^-$	PFSAs- Un	8	460.9334	C8F15SO3-	-0.7	99	Range: 15-16.2
<b>Ketone Perfluoroalkyl Sulphonate</b> $C_n F_{2n-1} SO_4^-$	PFSAs- Ketone	4	276.9411	C4F7SSO4-	-0.4	96	8.60
		5	326.9379	C5F9SO4-	-0.6	98	11.17
		6	376.9347	C6F11SO4-	-1.5	99	12.98
		7	426.9315	C7F13SO4-	-0.8	95	14.45
		8	476.9283	C8F15SO4-	-1.5	90	15.56
		9	526.9251	C9F17SO4-	-0.1	94	16.52
		10	576.9219	C10F19SO4-	0.8	86	17.15
		11	626.9187	C11F21SO4-	0.8	76	17.2-18.3
		12	676.9155	C12F23SO4-	-0.8	91	18.01-19.00
		13	726.9124	C13F25SO4-	0.4	98	18.50-19.50
<b>Perfluoroalkane sulfonamides</b> $C_n F_{2n+1} SO_2 NH$	FASAs	2	197.9654	C2F5SO2NH-	0.2	99	3.54
		3	247.9622	C3F7SO2NH-	0	99	9.03
		4	297.9589	C4F9SO2NH-	-0.3	99	12.355
		5	347.9557	C5F11SO2NH-	0.6	98	14.09 and 14.44
		6	397.9526	C6F13SO2NH-	-1.4	99	15.55; 15.64 and 15.92
		7	447.9494	C7F15SO2NH-	-2.8	98	16.79 and 17.11
		8	497.9462	C8F17SO2NH-	-1.4	99	17.74 and 18.07
		<b>Perfluoroalkyl sulfinates</b> $C_n F_{2n+1} SO_2^-$	PFSiAs	4	282.9481	C4F9SO2-	-0.9
5	332.9449			C5F11SO2-	-2.6	99	12.88
6	382.9417			C6F13SO2-	-1	98	14.13 and 14.44
7	432.9385			C7F15SO2-	-4.7	91	15.68
8	482.9353			C8F17SO2-	-0.1	93	16.44 and 16.72
<b>Perfluoroalkyl sulfonamidoethanols</b> $C_n H_5 F_{2n-3} NSO_3^-$	FASEs	4	241.9916	C4H5F5NSO3-	0	87	8.91
		5	291.9884	C5H5F7NSO3-	-0.8	90	12.08
		6	341.9852	C6H5F9NSO3-	-1.4	98	14.21
		7	391.9820	C7H5F11NSO3-	-3	99	15.42 and 15.76
		8	441.9788	C8H5F13NSO3-	-2.7	98	16.69 and 16.98
		9	491.9756	C9H5F15NSO3-	-2.1	76	17.98

		10	541.9724	C10H5F17NSO3-	-1.2	76	18.48 and 18.81
<b>Fluorotelomer sulfonates</b> <b>C<sub>n</sub>H<sub>4</sub>F<sub>2n-3</sub>SO<sub>3</sub>-</b>	FTSs	8	426.9679	C8H4F13SO3-	-0.9	100	15.30
		10	526.9615	C10H4F17SO3-	-0.4	99	17.38
<b>Fluorotelomer Thioamido Sulfonates</b>	FTSAS	6	602.0346	C15H17O5NS2F13-	0.8	91	15.36
<b>Perfluoroalkyl Sulfoamido Amines</b>	PFSaAm	6	483.0417	C11H12O2N2SF13-	-1	89	16.23
		8	583.0353	C13H12O2N2SF17-	-1.8	94	18.44

607 - (L): Linear isomer

**HIGHLIGHTS:**

- PFASs were investigated at a AFFF impacted fire training ground (FTG)
- AFFF impacted concrete and soil core samples (0-2m) were analysed by LC-QTOF-MS/MS
- Mass defect filtering strategy allowed the detection of untargeted PFASs
- Novel PFASs homologues were detected in soil and concrete samples collected at the FTG