# ENVIRONMENTAL CONTAMINATION AND ISOMER PATTERNS OF PFAAs AND 6:2 FTS CLOSE TO A FIRE-FIGHTING TRAINING FACILITY

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## Introduction

Perfluorinated alkyl acids are powerful surfactants and perfluorooctane sulfonates (PFOS) have been used in aqueous film forming foams (AFFFs) that are used to extinguish fires, particularly the difficult and critical ones such as petroleum fires. PFOS was mainly produced by 3M Company before 2002 using electrochemical fluorination. This process gives, as opposite to telomerisation, a mixture of branched and linear products. Norwegian regulations from 2005 banned PFOS in AFFFs, textiles and preservatives[1] as a step to phase-out perfluorinated chemicals and severely reduce emissions to the environment. Presented here is a screening of perfluoroalkylated acids (PFAAs) and 6:2 fluorotelomer sulfonic acid (6:2 FTS) in the environment of fire-fighting training facilities in Norway. Structural isomers if present were studied in samples from the point source (fire training ground) and further into the surrounding environment and biota.

## Materials and methods

*Chemicals*

Ammonium acetate (>99%, pa for HPLC) and *n*-hexane (Pestanal) were purchased from Fluka (Steinheim, Germany), HPLC-grade methanol (MeOH) was from Fisher Scientific (Leicestershire, UK). Acetonitrile (AcN) and water were from Lab-scan (Sowinskiego, Poland). Ammonium hydroxide ($NH_4OH$) 25%, sodium hydroxide (NaOH) p.a., sodium acetate p.a., hydrochloride acid (HCl) and glacial acetic acid (100%) were all purchased from E. Merck (Darmstadt, Germany). Native linear perfluorinated sulfonates (potassium perfluorobutanesulfonate (PFBS), sodium perfluorohexanesulfonate (PFHxS), sodium perfluorooctanesulfonate (PFOS), and sodium perfluorodecanesulfonate (PFDS)) and perfluorinated carboxylates (pentanoic- (PFPeA), hexanoic- (PFHxA), heptanoic- (PFHpA), octanoic- (PFOA), nonanoic- (PFNA), decanoic- (PFDA), undecanoic- (PFUnDA), dodecanoic- (PFDoDA), tridecanoic- (PFTrDA), and tetradecanoic acid (PFTeDA)) were from Wellington Laboratories (Guelph, Canada). Monomethyl- and dimethyl branched PFOS and PFOA standards were from Wellington Laboratories. Labeled standards were used as internal standards (added before extraction), also from Wellington Laboratories ($^{18}O_2$PFHxS, $^{13}C_4$PFOS, $^{13}C_2$PFHxA, $^{13}C_4$PFOA, $^{13}C_5$PFNA, $^{13}C_2$PFDA, $^{13}C_2$PFUnDA). *7H*-perfluoroheptanoic acid (7H-PFHpA) (98%) from ABCR (Karlsruhe, Germany) and $^{13}C_8$PFOA, (Wellington Laboratories) were used as recovery standards (added before injection). *1H,1H,2H,2H*-perfluorooctane sulfonate (6:2 FTS) (purity not given by supplier) was from Interchim (Montlucon, France).

*Samples*

Flesland airport is located in the western part of Norway near the city of Bergen and has a fire drill area. The area is connected to an oil separator and the seepage water is led to a lake and from the lake flows to the sea. Soil was sampled at the training ground, water was taken from the lake and sediment, fish liver, blue mussel and crab were

taken from the sea receiving waters from the fire drill area. Fish, mussels and crabs were pooled samples from 5 fish, 30 mussels and 5 crabs, respectively. Field blanks were taken for each matrix.

*Extraction and clean-up*

Soil, dry sediment and biota were stored at -20°C until analysis. Wet sediment was stored at 4°C until drying. Soil and sediment samples were air dried prior to extraction. All biological samples were homogenized before extraction (Ultra-Turrax, IKA). From the homogenate, 1 g of sample was taken in the analytical procedure.

The dried/homogenized soil/sediment/biological samples were added the internal standard (IS) mixture and 0.4 mL of a 0.2 M NaOH (in methanol) solution whereafter the samples were left for 30 min. Extraction was performed using 4 ml of AcN, ultrasonication for 15 min and shaking for 15 min. The samples were neutralized, centrifuged and the extraction was repeated once more and the two extracts were combined. Clean-up was performed with extraction three times with *n*-hexane (corresponding to a volume of 2:1 sample extract:hexane) and shaking with 50 mg dispersive carbon (Supelclean ENVI-Carb (20/400 mesh), Supelco Bellefonte, PA) and 100 µL glacial acetic acid. After filtration and evaporation the recovery standards (RS) *7H*-PFHpA and $^{13}C_8$-PFOA were added together with 2mM ammonium acetate (aq). Blank samples (extraction blanks) and field blanks where performed in parallel with each batch of samples, and were treated in exactly the same manner as the other samples.

Water samples (200-500 mL) were filtered through glass microfiber filters (GF/B, Whatman) before extraction using Oasis WAX (6cc/150mg, Waters, Milford, MA, USA) according to standard method ISO 25101 [2]. Internal standard mixture was added before extraction. The WAX cartridges were conditioned before vaccum was used to run through the water samples at a flow rate of approximately 1 drop per second. Sodium acetate buffer (4 mL, 0.025 M) was added and the eluate was discarded. After drying the cartridges using vacuum suction 4 mL methanol was added and discarded and the analytes were then eluted with 4 mL of 0.1 % $NH_4OH$/methanol solution at a rate of one drop per second. The eluates were collected, filtrated and evaporated to suitable volume with a gentle stream of nitrogen gas. Recovery standards ($^{13}C_8$-PFOA, *7H*-PFHpA) and ammonium acetate (aq) were added to the final extract. Extraction and field blank samples were prepared with ultra-pure laboratory produced water and were treated exactly in the same way as the samples.

*Chemical analysis and quality assurance*

Analysis was performed using an Acquity UPLC coupled to a Quattro Premier XE MS/MS (Waters Corporation, Milford, US) with an atmospheric electrospray interface operating in negative ion mode (ES-MS/MS). Multiple reaction monitoring was used monitoring two product ions for each compound. Concentration of the analytes in the samples was calculated using internal standard quantification. The internal standard closest in retention time was used for those compounds that did not have a corresponding labeled internal standard (PFBS, PFDS, 6:2 FTS, PFPeA, PFHpA, PFTrDA, PFTeDA). Separation was performed on an Acquity BEH C18 2.1 x 50 mm (100 mm for isomer analysis), 1.7 µm kept at 50°C. An extra guard column (PFC isolator, Waters Corporation, Milford, US) was inserted between the pump and injector to trap contaminants originating from the LC system. Injection volume was 10 µL and the flow rate was set to 400 µL/min (300 µL/min for isomer analysis). A gradient program was employed delivering mobile phases consisted of 2 mM ammonium acetate in methanol, and 2 mM ammonium acetate in water for quantification, and water/methanol/acetonitrile/2mM ammonium acetate for isomer analysis.

The limit of detection (LOD) was set to three times the noise level. If trace levels were found in extraction blanks the LOD was set to 3xblank signal. Two transitions were measured and the ratio between the qualifier and quantifier ions was calculated and samples with more than 50% difference were not quantified. The recoveries of the internal standards were monitored and native compounds were spiked to clean matrices. Acceptable recoveries were 50-

150%. Results with less certainty were obtained for some compounds in soil (25-50% recovery) and 6:2 FTS were not quantified in mussels and crab due to signal enhancement and lack of proper internal standard.

**Results and discussion**

The environment around the fire training ground was clearly contaminated from a mixture of PFAAs, elevated sulfonates, carboxylates and 6:2 FTS were seen in soil and receiving water. Bioaccumulation in fish liver had taken place by PFOS, 6:2 FTS, PFDS and longer chain carboxylates like PFTrDA.

Soil at the fire fighting training ground contained 612 ng/g d.w. 6:2 FTS and 273 ng/g d.w. PFOS. Lower levels of PFBuS, PFHxS, PFDS, and carboxylates C5-C8, C11, C12 were also detected (up to 6 ng/g d.w.). Even higher levels were quantified in soil 10 m from the training ground (2101 ng/g 6:2 FTS and 1905 ng/g PFOS). The levels thereafter decreased with increasing distance.
The receiving water (n=3) contained a suite of sulfonates and carboxylates. Highest levels were for 6:2 FTS (5110-6693 ng/L) followed by PFOS (1427-2078 ng/L). Carboxylates with carbon chain length C5-C8 were average between 155-560 ng/L but also C9-C11 were detected (3.8-28 ng/L). PFBuS was on average 97 ng/L.
Sediment from three locations contained PFOS between 35 and 88 ng/g d.w., 6:2 FTS was on average 7 ng/g d.w. but the second highest levels was found for PFUnDA (average 15 ng/g d.w.). Lower contamination was seen for the other studied compounds except for PFOA, PFNA and PFTDA that were <LOD.
Only PFTrDA was found in mussel (average 0.41 ng/g f.w.) and low levels were also found in crab with PFOS having the highest concentration (average 2.3 ng/g f.w.) followed by PFTrDA (average 1.3 ng/g f.w.). Fish liver (f.w.) contained more compounds at higher concentrations, average values (n=4) 2281 ng/g PFOS, 160 ng/g 6:2 FTS, 101 ng/g PFUnDA, 52 ng/g PFDS, 44 ng/g PFTrDA.

The isomer pattern of PFOS in soil was 63% linear PFOS (L-PFOS) at the training ground (0 m), assuming an ECF contamination source (Figure 1). The percentage L-PFOS thereafter increased up to 85% linear at 100 m from the center. 6-monometyl branched PFOS and the cluster of 3/4/5-monomethyl branched PFOS were the highest level branched isomers. The isomer pattern thereafter changed in the receiving water body to 58-61% L-PFOS. In fish liver a percentage of 87-90% L-PFOS was seen. The contrary was seen for 6:2 FTS that only showed one single peak thus suggesting a telomerisation source. Isomers were also detected for PFBuS and PFOA in water and for PFDS in fish and soil. The different environmental behavior for branched and linear isomers as suggested here could be linked to differences in soil sorption and water solubility.

**Acknowledgment**

This study was originally part of a larger study performed on behalf of Climate and Pollution Agency (Klima- og forurensningsdirektoratet, KLIF). http://www.klif.no/publikasjoner/2625/ta2625.pdf

**References**

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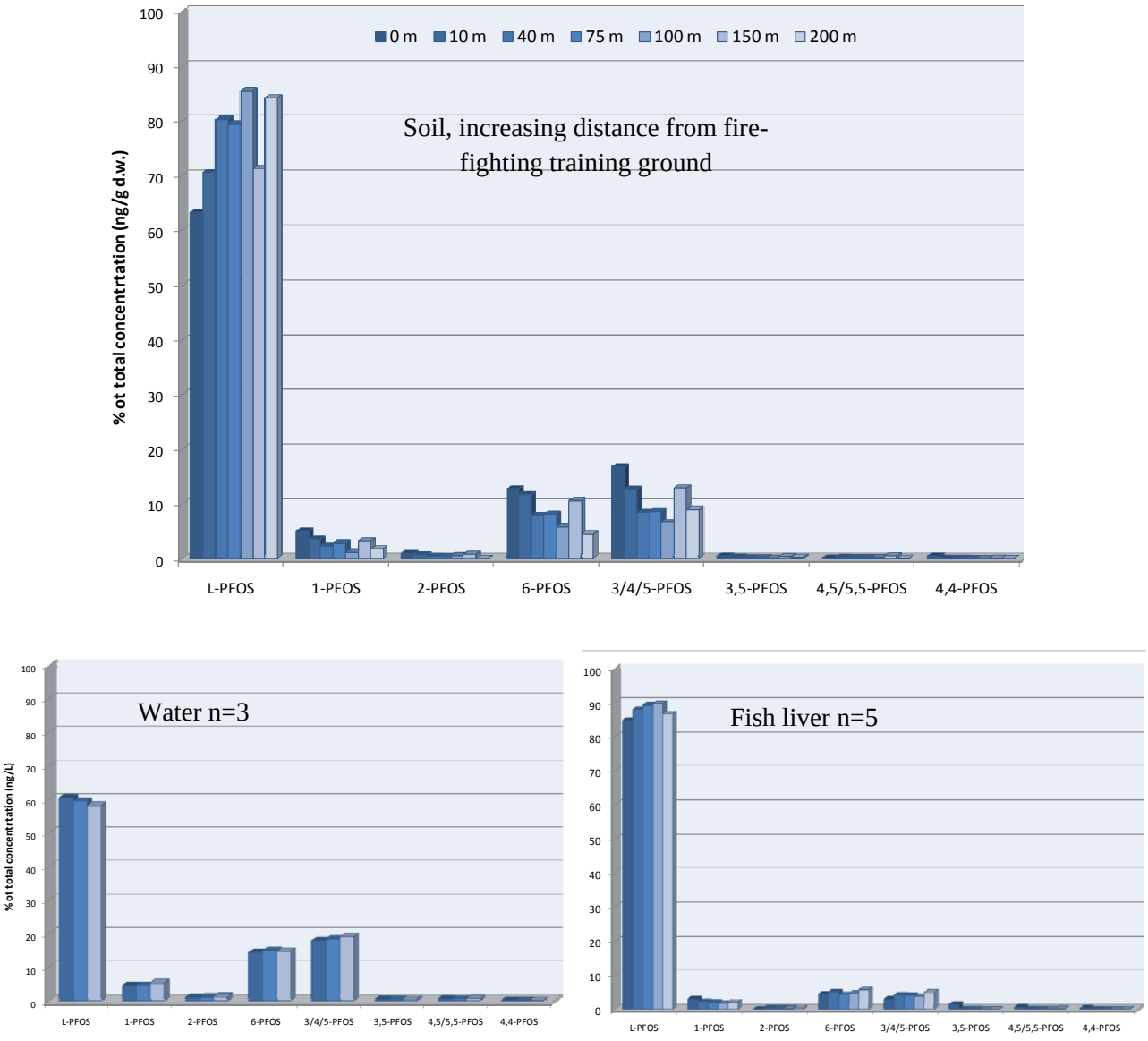


**Figure 1.** PFOS isomer pattern in the environment close to fire-fighting training facility. Soil from airport training platform and vicinity, receiving water and fish livers from the receiving sea.