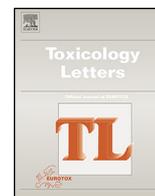




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## Firefighters' exposure to perfluoroalkyl acids and 2-butoxyethanol present in firefighting foams

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### HIGHLIGHTS

- PFOA and PFOS were present in Sthamex AFFF 3% in all trainings.
- Fire fighters' serum PFHxS and PFNA elevated after three consecutive trainings.
- Urinary BAA concentration exceeded the limit of occupationally unexposed population.
- Elevated concentrations reflected dermal or oral exposure to PHAS and EGBE.
- Non-fluorine based and the alcohol resistance properties were favored in AFFFs.

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### ABSTRACT

The aim of this study was to assess eight firefighters' exposure to Sthamex 3% AFFF (aqueous film forming foam) in the simulation of aircraft accidents at Oulu airport in Finland. Study was conducted in 2010 before limitation for the use of PFOA and PFOS in AFFFs. Due to prospective limitation also eight commercially available AFFFs were evaluated from occupational and environmental point of view to find substitutive AFFFs for future. The firefighters' exposure to twelve perfluoroalkyl acids (PFAS) was analyzed in order to observe the signs of accumulation during three consecutive training sessions. The firefighters' short-term exposure to 2-butoxyethanol (EGBE) was analyzed by urinalysis of 2-butoxyacetic acid (2-BAA). For the background information also the concentration of PFAS in used AFFF-liquid was analyzed. Fire fighters' serum PFHxS and PFNA concentrations seemed to increase during the three training sessions although they were not the main PFAS in used AFFF. The statistical significance for the elevations was not able to test due to limited size of test group. In two training sessions, the average urinary excretions of 2-BAA exceeded the reference limit of the occupationally unexposed population. In the evaluations of the firefighting foams, non-fluorine based products were favored and the alcohol resistance properties of foams were recommended for consideration due to the increasing use of biofuels.

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### 1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are a subgroup of per- and polyfluorinated alkyl substances (PFAS). These substances have been widely used in many industrial and commercial applications. The chemical and thermal stability of a perfluoroalkyl moiety, which is caused by the very strong C–F bond, in addition to

its hydrophobic and lipophobic nature, lead to highly useful and enduring properties in surfactants and polymers (Fromme et al., 2009).

One of the surfactant applications is in aqueous film-forming foams (AFFFs) used to extinguish hydrocarbon-fuel and chemical solvent fires. The foams acts to both cool the fire and to coat the fuel, preventing its contact with oxygen. This can happen with the help of PFAA compounds or fluorotelomers and hydrocarbon surfactants such as sodium alkyl sulfate (Oakes et al., 2010; Place and Field, 2012). They form a film of aqueous solution covered on both sides by monolayers of mixed surfactants (Moody and Field, 2000). Other common ingredients in AFFFs are solvents, of which the most

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common are 2-butoxyethanol (EGBE), 2-(2-butoxyethoxy) ethanol (DEGEBE) and 1,2-ethanediol (EG), which are required for the stabilization of the surfactants and foam, and they also act as anti-freezing agents (Moody and Field, 2000; Paloposki, 2013).

Studies with PFAAs have shown that these compounds may increase total and LDL cholesterol as well as the risk of breast cancer (Nelson et al., 2009; Steenland et al., 2009; Frisbee et al., 2010; Bonfeld-Jorgensen et al., 2011). Recently, it has been shown that there is a link between the exposure to PFAAs and the disruption of thyroid hormones (Bloom et al., 2010; Lopez-Espinosa et al., 2012). This is a very important finding concerning firefighters' exposure to AFFFs. Similar effects have been found in firefighters' exposure to fire retardant (Shaw et al., 2013). These compounds together might have additive or even synergistic effects on firefighters' thyroid hormones.

Dietary intake is believed to be the major exposure route for PFAAs in the general adult population (Fromme et al., 2009; Haug et al., 2011). In addition to food and environmental background exposure to PFAAs, an occupational exposure can play an important role in total exposure (Fromme et al., 2009). During the suppression of a liquid fire, firefighters may be exposed to AFFFs through inhalation and dermal exposure routes. Contaminated personal protective equipment and firefighting suits might also increase the risk of hand-to-mouth transfer and eventual exposure via the gastrointestinal tract. The washing of these equipment is still a big problem for fire brigades in Finland and the use of contaminated firefighting suits is a very common practice. Thus, firefighters' short and also long term occupational exposure to PFAA compounds seems to be more than evident.

Due to persistence and bioaccumulative properties, including the potent harmful and toxic effects of PFOA and PFOS, the EU decided to ban their use in the majority of applications, including AFFFs. In June 2012 fire brigades were required to stop using of AFFFs containing PFOS and PFOA. The banning of PFOS and PFOA raised the question in fire brigades: What replacement options are there for firefighting foams in future? On the other hand, there was a need to estimate firefighters' exposure to AFFFs in training simulations of aircraft accidents.

In this study, firefighters' exposure to 12 PFAAs and EGBE was assessed by biomonitoring methods during three consecutive firefighting training sessions in 2010 at the Oulu airport in Finland. Sthamex 3% AFFF was used as the extinguishing foam for jet fuel fires during training. Additionally, eight commercially available firefighting foams in Finland were evaluated from occupational, environmental and technical points of view in order to find possible replacements for the future.

## 2. Materials and methods

### 2.1. Study subjects

This study was carried out during training for the suppression of liquid fires in aircraft accident simulations. Eight male firefighters from the Oulu Airport Fire Brigade in Finland participated in three consecutive training sessions held over a three month period in 2010. In each training simulation the length of individual firefighters' smoke diving sessions varied from 60 to 63 min. These training sessions were carried out in a conventional aircraft accident simulator and in training fire-pits. Smoke and heat were generated by burning jet propulsion fuel in the pools and wooden pallets in the simulator. Firefighters performed two smoke dive tasks per training session. All test days followed the same protocol. Sthamex 3% AFFF was used for fire suppression. This foam contained perfluorinated surfactants and EGBE. The profile of PFAA-compounds in the foam liquid used was determined by LC–MS/MS analyses for each training session. In addition to their firefighting suits, gloves and boots, the firefighters used full-face masks and breathing air was supplied via compressed air bottles (Dräger). The average age of the firefighters' was  $44.4 \pm 12.4$  years (mean and standard deviation). The training schedule was as follows: The firefighters extinguished the jet fuel fire in the training fire-pits and then they rescued survivors from the aircraft accident simulator. After that, they cleaned the training pools by removing the used firefighting foams from the training fire-pits. The firefighters performed these three tasks twice during each training session. The final work task after each session was the maintenance of used fire hoses, fire foam trucks and personal protective equipment.

The blood sampling was performed at four time points. Baseline samples were taken two weeks before the first training session. The next three samples were taken two weeks after each training session. A nurse from the occupational health care unit in Oulu took all blood samples and delivered them to the National Institute for Health and Welfare laboratory. Urine samples were collected immediately before and after each training session. Samples were stored at  $-21\text{ }^{\circ}\text{C}$ , until the analysis and samples were delivered to the Finnish Institute of Occupational Health laboratory.

The Ethics Committee of the Hospital District of Helsinki and Uusimaa, approved the study (reference number 227/13/03/04/2009). Written informed consent was obtained from all participants.

### 2.2. Foams selected for the evaluation

Eight firefighting foams commercially available in Finland were selected for the evaluation study. The evaluation was done from

**Table 1**  
Ingredients and freezing points of firefighting foams according to their material safety data sheets.

FFF	1.	2.	3.	4.	5.	6.	7.	8.
Solvent	EGBE	EGBE	DEGEBE	EGBE	DEGEBE	DEGEBE	DEGEBE	DEGEBE
Amount of solvent, %	<5	8–10	15–40	<8	<20	<20	5–10	<20
Anti-freezing agent				EG	EG			
Amount of anti-freezing agents, %				< 20	< 20			
Surfactant	Fluorinated and synthetic	Starch and sucrose	Compounds made from fatty acids	Synthetic				
Freezing point, C	–8	–15	–15	–15	–18	–8	–16	–3
Type of PFAAs	PFAAs	PFAAs	Fluoro-telomer	Fluoro-telomer	Fluoro-telomer	PFAA free	PFAA free	PFAA free

Firefighting foams: 1. Sthamex AFFF 3% (Sthamer GmbH & Co., KG, Germany); 2. Afrofilm AFFF 3% (Germania Feuerschutz GmbH, Germany); 3. Towalex AFFF universal 3–6% (total Walther Feuerschutz Löschnittel GmbH, Germany); 4. Moussol-APS 3%, AFFF, FFFP, AR (Sthamer GmbH & Co.KG, Germany); 5. Artic foam 602 ATC 3–6%, AFFF, AR (Solberg Scandinavian AS, Norway); 6. Re-healing foam RF3X6 ATC 3–6%, AFFF, FFFP (Solberg Scandinavian AS, Norway); 7. Bio ex Ecolpol FFF AR 3 (Bio-EX SA, France); 8. Solberg TF5X, training foam (Solberg Scandinavian AS, Norway); solvents and anti-freezing agents; EGBE: 2-butoxyethanol; DEGEBE: 2-(2-butoxyethoxy)ethanol; EG: 1,2-ethanediol.

occupational hygiene, environmental and technical points of view based on information in the material safety data sheets of each product and on chemical data in literature. All of the selected firefighting foams are described in Table 1. In the evaluation, close attention was paid to the amounts and properties of the solvents and anti-freezing agents, the types of surfactants, the freezing points of liquids and also the types of perfluorinated compounds used.

### 2.3. Chemicals and reagents used in the 2-BAA analysis

A standard BAA (97%) compound for 2-BAA analysis was purchased from Tokyo Kasei (Tokyo, Japan). An internal standard, 2-pentoxoacetic acid PAA (95%) was not commercially available, so it was synthesized at the University of Eastern Finland. Methanol was purchased from Rathburg (Walkersburn, Scotland). Sulfuric acid (95–97%), hydrochloric acid (37%), ethyl acetate and dichloro-methane were purchased from Merck (Darmstadt, Germany).

### 2.4. BAA analysis

The urinalysis was carried out using a gas chromatograph equipped with a flame ionization detector. The column was a high-performance cross-linked methyl silicone gum capillary column (HP-5) (length 50 m, I.D. 0.32 mm, film thickness 0.52  $\mu\text{m}$ ) (Avondale, PA, USA). The extraction procedure, instrumental conditions and validation of the method has been described in our earlier publication (Laitinen, 1997). The urinary results of 2-BAA were corrected using urinary creatinine determined with the alkaline picric acid method. Urine samples were collected immediately before and after the work shift. They were stored at  $-21\text{ }^{\circ}\text{C}$ , until the analysis. The results of the urinary 2-BAA were reported as mmole 2-butoxyacetic acid per mole creatinine. The limit of quantifications (LOQ) for BAA was 0.5 mmol/mol creatinine and limit of detection (LOD) 0.1 mmol/mol creatinine. The recovery of BAA was 95% at concentration level of 30 mg/L (Laitinen, 1997).

### 2.5. Chemicals and reagents used in the PFAA analysis

Methanol (HPLC grade), methyl tert-butyl ether, tetrabutylammonium hydrogen sulfate and sodium hydroxide were obtained from J.T. Baker (Deventer, the Netherlands). Sodium carbonate was obtained from Merck (Darmstadt, Germany), newborn calf serum (NBCS) from the Gibco/Invitrogen Corporation (Auckland, New Zealand), and *N*-methylpiperidine from Sigma–Aldrich (St. Louis, MO, USA). All the native PFAAs, i.e., perfluorohexanoic acid (PFHxA), -heptanoic acid (PFHpA), -octanoic acid (PFOA), -nonanoic acid (PFNA), -decanoic acid (PFDA), -undecanoic acid (PFUnA), -dodecanoic acid (PFDoA), -tridecanoic acid (PFTriA), -tetradecanoic acid (PFTeA), -hexanesulfonate (PFHxS), -heptanesulfonate (PFHpS), -octanesulfonate (PFOS) and -decanesulfonate (PFDS) were acquired from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Isotope labeled PFAAs (abbr. MPFAA) were used as internal standards. MPFOA (1,2,3,4- $^{13}\text{C}_4$ ), MPFNA (1,2,3,4,5- $^{13}\text{C}_5$ ), MPFUnA (1,2,3,4,5,6,7- $^{13}\text{C}_7$ ), MPFDoA (1,2- $^{13}\text{C}_2$ ), MPFHxS (18O2) and MPFOS (1,2,3,4- $^{13}\text{C}_4$ ) were obtained from Wellington Laboratories Inc., and MPFDA (1-9- $^{13}\text{C}_9$ ) were obtained from CIL (Andover, MA, USA).

### 2.6. Analysis of PFAAs

Prior to an analytical procedure, a 10 ng of mass labeled internal standards for quantitation were added into the samples. A 0.5 mL serum sample or a 1 mL AFFF sample was extracted twice after ion-pair formation with 3 mL of MTBE according to the protocols by Hansen et al., (2001). The extract was evaporated to dryness under a nitrogen flow and reconstituted to 300  $\mu\text{L}$  of 60% aqueous

methanol. Prior to instrumental analysis, the samples were filtered with a 0.2  $\mu\text{m}$  syringe filter (Pall Life Sciences, Ann Arbor, MI). The PFAAs were analyzed using liquid chromatography negative ion electrospray tandem mass spectrometry (LC–ESI–MS/MS). The details of the LC–MS parameters have been presented earlier by Koponen and co-workers and the quantitation was based on the method in the same study (Koponen et al., 2013). The concentrations of PFAAs in serum are reported as ng/mL and in AFFF liquids  $\mu\text{g}/\text{mL}$ . The LOQ for PFAAs in serum and in AFFF analysis were 0.35 ng/mL and 20  $\mu\text{g}/\text{mL}$ , respectively. For PFAAs analyses no percent recoveries for contaminants were able to determined, since the recovery standards were not commercially available at the time of the analysis.

## 3. Results and discussion

### 3.1. PFAA concentrations in AFFF liquids

The concentrations of PFAAs in the Sthamex 3% AFFF liquid used in all trainings were analyzed. The most abundant PFAAs in the AFFFs were PFOS and PFOA, which is in agreement with a previous study (Backe et al., 2013). The detected average concentrations of PFOS and PFOA in the Sthamex 3% AFFF liquid were 240  $\mu\text{g}/\text{mL}$  and 21  $\mu\text{g}/\text{mL}$ , respectively. Low concentration of PFHxA and PFNA were also detected, but the concentrations were below the LOQ (limit of quantification).

### 3.2. PFAA concentrations in serum

Total serum PFAA concentrations in this study population ranged from 6.5 to 51 ng/mL. The median and range for the main serum PFAAs (PFOS, PFOA, PFNA and PFHxS) concentrations during three consecutive trainings are shown in Table 2. In the general Nordic population, the concentrations are expected to be in the range of 3.9–27 ng/mL for PFOS, 0.76–5.01 ng/mL for PFOA, 0.35–1.66 ng/mL for PFNA, and 0.73–10.3 ng/mL for PFHxS (Haug et al., 2009; Bjermo et al., 2013). Occupationally exposed employees usually have very high serum PFAA concentrations as compared to non-occupationally exposed populations. For example in another study the geometric mean serum PFOS concentrations for employees of two perfluorooctanyl manufacturing locations were between 440 and 910 ng/mL (Olsen et al., 2003). The PFOA values for these same employees were between 330 and 1130 ng/mL.

### 3.3. Urinary 2-BAA concentrations

All firefighters' urinary 2-BAA excretions were below the LOQ after the first training session (Fig. 1). In the second training session 50% of the urinary excretions after exposure exceeded the limit of

**Table 2**

Firefighter' medium serum concentration of the main PFAAs and urinary BAA and also the range of the results in three consecutive trainings.

Compound	Serum concentration(ng/mL)	
	Median	Range
PFOS	11.1	2.79–35.8
PFHxS	2.19	1.05–4.30
PFOA	2.94	1.61–4.85
PFNA	1.22	0.43–6.69
Total PFAAs	18.4	6.54–51.2

	Urinary concentration (mmol/mol creatinine)	
	Median	Range
BBA (before exposure)	<0.5	<0.5
BBA (after exposure)	<0.5	<0.5–2.7

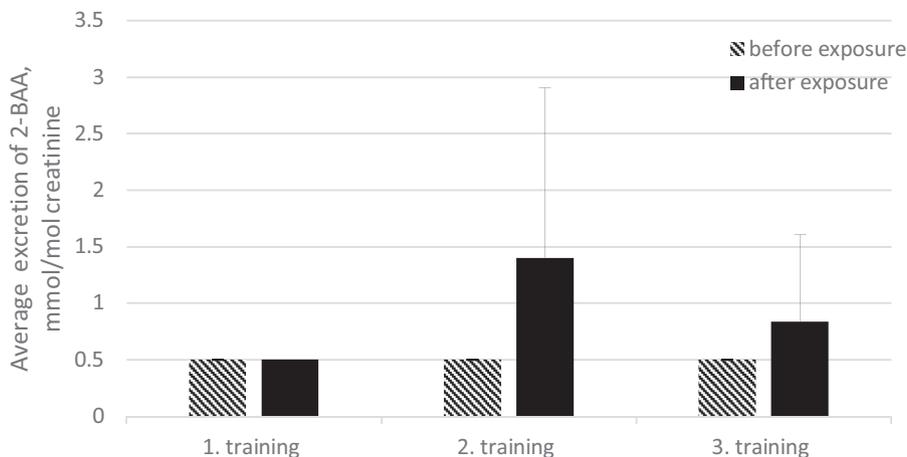


Fig. 1. Average and standard deviation of urinary 2-butoxyacetic acid excretions before exposure and immediately after exposure.

unexposed population in Finland (0.5 mmol/mol creatinine). An average concentration after exposure was 1.4 mmol/mol creatinine and the standard deviation of results was 1.5 mmol/mol creatinine. After the third training session 25% of the urinary excretions exceeded the limit of occupationally unexposed population. The average concentration after exposure was 0.8 mmol/mol creatinine and the standard deviation was 0.8 mmol/mol creatinine. All concentrations before all training sessions were under the LOQ. The measured concentrations after exposure were far below the biological action limit value in Finland for 2-BAA (60 mmol/mol creatinine) and they showed moderate exposure to 2-butoxyethanol (Fig. 1). The median and range concentrations of BAA measured before and immediately after exposure remained under LOQ during three consecutive trainings. The highest BAA concentration 2.7 mmol/mol creatinine was measured after second trainings (Table 2).

3.4. The effect of exposure to PFAAs and EGBE during training sessions on urinary and serum levels

The hypothesis of this study was that PFAAs might accumulate in firefighters' bodies during the three month training period. That

would be possible to see as elevated serum concentrations of PFAAs in samples taken two weeks after each training session compared to the concentrations in baseline samples taken two weeks before the first training session. The firefighters' short term exposure would be possible see in their elevated urinary excretions of 2-BAA taken immediately after a training session compared to the baseline samples taken before exposure.

After each of the three training sessions the concentrations of PFAAs were analyzed and the respective concentrations were compared to baseline sample concentrations. Accumulation of the main serum PFAAs (PFOS, PFOA, PFNA and PFHxS) are shown in Fig. 2. The relative concentrations of the main PFAAs seemed to be higher after the entire training period. The highest increases of 17 and 10% were observed with PFHxS and PFNA, respectively. Statistical significance for the difference in the beginning and end of the study was not able to carry out due to the limited size of test group. It was interesting to note that the concentrations of PFHxS and PFNA were the most elevated, despite the fact that the concentration of both PFHxS and PFNA were below the LOQ in used the Sthamex 3% AFFF liquid. Measured PFNA concentration exceeded the LOD, but stayed under LOQ in Sthamex 3% AFFF liquid. According to that fire fighters' moderate PFNA exposure

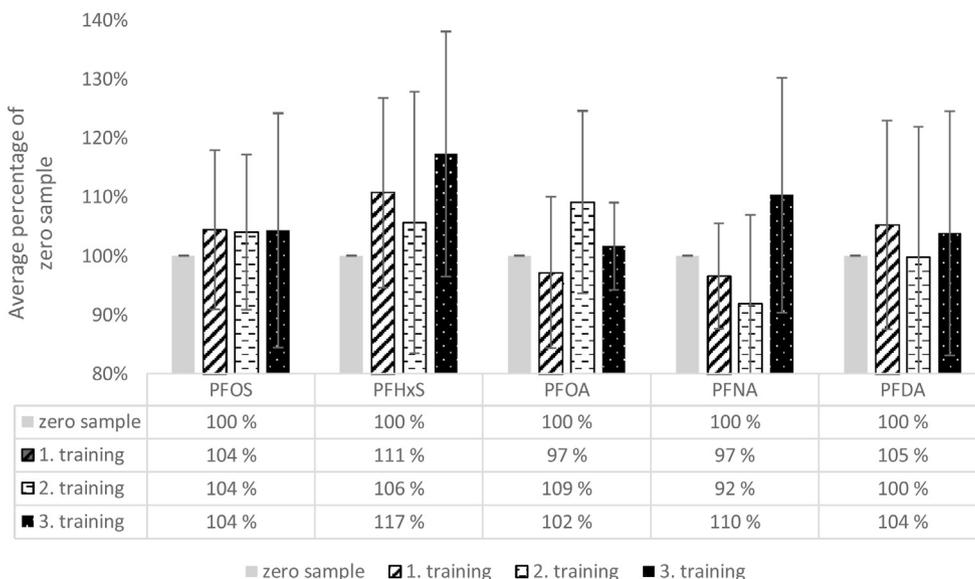


Fig. 2. Average and standard deviation of PFAA compounds in firefighters' serum during the three month training period.

source was available in used firefighting foam. Because we could not detect any PFHxS from firefighting foam liquid, there have to be another sources for it. Our finding are consistent with the results from earlier published papers, where have also been detected elevated PFAS concentrations among fire fighters (Tao et al., 2008; Jin et al., 2011). Another possible explanation for elevation of PFHxS could be thermal decomposition of longer chain fluorotelomers in jet propulsion fuel fire, which can provide shorter chain PFAS such as PFHxS, but information about that is still limited (Yamada et al., 2005).

The urinary 2-BAA levels measured in firefighters also showed moderate exposure to EGBE and supports the finding of PFAAs. Due to the firefighters' heavy protection against inhalation exposure, these results seem to indicate that dermal exposure plays a role in firefighters' total exposure. Fire fighters' dermal exposure has been studied during last decade and skin has ranked more and more important exposure route (Fent et al., 2013). The potential of PFAS to expose through the skin has been tested with animals in the laboratory and results showed that PFAS compounds might absorb through the skin (Franko et al., 2012). The other possible exposure route is transfer from contaminated personal protective equipment to hands and finally from hands to mouth, leading to exposure through the gastrointestinal system (Fent et al., 2013).

### 3.5. The evaluation of eight commercially available firefighting foams from occupational hygiene, environmental and technical points of view

From an occupational hygiene point of view, the best solvent of the evaluated foams was DEGBE. This is because it has the lowest vapor pressure, which means the lowest potential to expose the user via inhalation. The acute effects of DEGBE are irritation of the eyes and skin, but due to the higher vapor pressure of EGBE its acute effects are irritation of the respiratory system and CNS symptoms (Lundberg, 1995). High exposure to 1,2-EG can cause hazardous kidney effects, such as kidney stones, metabolic acidosis and renal failure. Glycolic and oxalic acids, the metabolites of 1,2-EG, are responsible for these effects (Kohri et al., 1991; Laitinen et al., 1996).

From the environmental and occupational hygiene points of view the PFAA compounds used pose a potential risk for accumulation both in the workers and in the environment. They are very persistent, having very long elimination times such as 5, 4 and 9 years for PFOS, PFOA and PFHxS, respectively (Olsen et al., 2003). Similar elimination times have also been reported for PFNA (Nilsson et al., 2010). Many manufacturers have replaced PFOA and PFOS with fluorotelomers. In degradation studies however, it has been noticed that longer chain fluorotelomers might metabolically, through microbial and atmospheric processes degrade to PFNA or even PFOA (Ellis et al., 2004). This poses important questions for the future about the safety of fluorotelomers. Due to that, manufacturers of fluorotelomers have started to pay more attention to the purity of their manufacturing processes and shorter chained fluorotelomers are favored in the production of AFFFs (Seow 2013; Paloposki, 2013).

From the technical point of view, especially in Nordic countries, the freezing point of the AFFF liquid is very important. Additionally, new biofuels containing significant amounts of alcohols pose a challenge for conventional AFFF foams. In the future, alcohol resistant (AR) foams will be needed in the suppression of jet propulsion fuel fires (Paloposki et al., 2005; Paloposki, 2013). According to the evaluation of eight firefighting foams commercially available in Finland, Bio Ex Ecopol 3 × 3//3 × 6 best fulfilled all these requirements (Table 1).

## 4. Conclusions

The PFHxS and PFNA levels seemed to increase, after the three consecutive training sessions compared to the firefighters' individual baseline concentrations in samples taken two weeks before the first exposure period. Statistical significance between PFAS levels in the beginning and end of the study was not able to carry out due to the limited size of test group. Interesting was note that elevated PFAS levels were not the main PFAS in used AFFF. Explanation for that might be the other PFAS source than firefighting foam or decomposition of longer chain fluorotelomers in AFFF in jet propulsion fuel fire.

The average excretions of 2-BAA exceeded the reference limit of occupationally unexposed population in samples taken after the second and third training sessions. The average levels of 2-BAA varied from 1.3 to 2.3% of the biological action limit value for BAA, which demonstrated the firefighters' moderate exposure to firefighting foams. Due to the firefighters' heavy inhalation protection, these results seemed to reflect a potential dermal or oral exposure risk to firefighting foams in the suppression of jet propulsion fuel fires. This have to take account in designing new personal protective equipment for fire fighters. The best biological indicator of exposure to firefighting foams seems to be the solvent or anti-freezing agents used. Example of that is EGBE and its biological indicator BAA, which one was used in our study.

In the evaluation of the firefighting foams, non-fluorine based foams were favored from occupational hygiene and environmental points of view. The alcohol resistance properties of foams should also be taken into account due to the increased use of biofuels. In the selection of future firefighting foams it is also essential to consider their freezing points as well as their efficiency in suppressing liquid fires. According to the evaluation of eight firefighting foams commercially available in Finland, Bio Ex Ecopol 3 × 3//3 × 6 best fulfilled all these requirements.

## Conflict of interest

The authors declare that there are no conflicts of interest.

## Transparency document

The Transparency document associated with this article can be found in the online version.

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