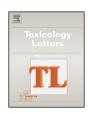
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# Firefighters' exposure to perfluoroalkyl acids and 2-butoxyethanol present in firefighting foams



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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 (DEGBE) 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; Bonefeld-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 PFOS 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  $-21\,^{\circ}\text{C}$ , 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	DEGBE	EGBE	DEGBE	DEGBE	DEGBE	DEGBE
Amount of solvent, %	<5	8-10	15-40	<8	<20	<20	5-10	< 20
Anti-freezing agent				EG	EG			
Amount of anti-				< 20	< 20			
freezing agents, %								
Surfactant	Fluorinated and	Starch and	Compounds made	Synthetic				
	synthetic	synthetic	synthetic	synthetic	synthetic	sucrose	from fatty acids	
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 Ecopol FFF AR 3 (Bio-EX SA, France); 8. Solberg TF5X, training foam (Solberg Scandinavian AS, Norway); solvents and anti-freezing agents; EGBE: 2-butoxyethanol; DEGBE: 2-(2-butoxyethoxy)ethanol; EG: 1,2-ethanediol.

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