



Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams



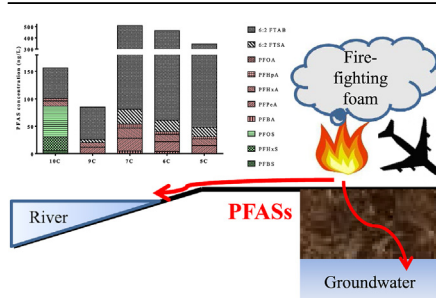
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HIGHLIGHTS

- Firefighting foam concentrates contained a mixture of different fluorotelomers.
- A precursor oxidation assay revealed the presence of unidentified fluorotelomers.
- PFASs were measured in water around four sites impacted by firefighting activities.
- PFAS profiles suggested different routes of transport from the foam usage area.

GRAPHICAL ABSTRACT



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ABSTRACT

To extinguish large-scale fuel fires, fluorosurfactant based foams (FSBFs) were developed in the 1960s and have been used ever since. In this study, 154 per- and polyfluoroalkyl substances (PFASs) including 122 emerging PFASs used as surfactants in FSBFs were sought in nine different foam concentrates. Field investigations were also carried out in the vicinity of four sites where FSBFs are or were intensively used (two airports, a training center for firefighters and an oil storage depot after a large explosion).

In the foam concentrates, only three PFASs were quantified with concentrations ranging from 22,500 to 3,188,000 µg/L. Thirteen emerging PFASs were also identified in these samples based on their mass transitions and intensities. Overall, each foam was a mixture of at least two classes of PFASs. In three concentrates, none of the 122 emerging PFASs were identified as the main ingredient. A perfluoroalkyl acid precursor oxidation assay was therefore performed, and revealed the presence of high amounts of unidentified PFASs.

In the vicinity of the four investigated sites, several PFASs were systematically quantified in all of the samples collected downstream of the sites. PFAS profiles were heavily influenced by parameters such as route of PFAS transport after use (runoff, seepage, direct discharge), time elapsed since the cessation of firefighting activities, and firefighting foam composition. The PFAS concentrations found around the investigated sites are the highest recorded in France and resulted in the closure of certain drinking water resources.

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1. Introduction

Fluorosurfactant based foams (FSBFs) have been used since the 1960s to extinguish fuel-based fires (i.e. gasoline and kerosene).

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They are used during incidents such as large storage tank fires (Rumsby et al., 2009; Taniyasu et al., 2015) and aircraft crashes (Oakes et al., 2010), but also during regular training exercises (Baduel et al., 2015; SFT, 2008). In some cases, they have also been employed for combating large-scale fires involving articles in stores (Weber et al., 2010). They are widely and routinely used by firefighters at military and civilian airports (Ahrens et al., 2015; Backe et al., 2013; Gewurtz et al., 2014; Moody et al., 2002, 2003), oil refineries (Weiss et al., 2012) and municipal fire departments (Moody and Field, 2000).

Five kinds of firefighting foams are commonly used (Nordern, 2013): fluoroprotein foams (FPs), aqueous film-forming foams (AFFFs), film-forming fluoroprotein foams (FFFPs), alcohol-resistant aqueous film-forming foams (AR-AFFFs) and alcohol-resistant film-forming fluoroprotein foams (AR-AFFFPs). All of them were designed to be effective in dealing with specific fire conditions, and contain one or more fluorinated surfactants as a key ingredient.

Fluorinated surfactants decrease surface tension and are thermally stable. Therefore, they allow a thin film to spread out and float on the fuel's surface. This substantially improves the foam's fire knockdown efficiency as it creates an effective fuel vapor barrier that extinguishes the fire. The foam minimizes the evaporation of flammable solvents and the fluorinated surfactants help it completely and stably cover the fuel's surface, thus preventing recognition.

Fluorinated surfactants belong to the per- and polyfluoroalkyl substances chemical family (PFASs). The types of PFASs in FSBFs vary by year of production and manufacturer. From approximately 1965 to 1975, perfluorinated carboxylic acids (PFCAs), a sub-group of PFASs, were used in FSBFs (Prevedouros et al., 2006). From the 1970s, the 3M company dominated the market with FSBFs containing perfluorooctane sulfonate (PFOS) and PFOS derivatives (Paul et al., 2009). The other manufacturers at that time used fluorotelomer-based surfactants. On May 16, 2000 3M announced the phasing out of PFOS chemicals due to health and environmental concerns. It is sometimes claimed that fluorotelomers (FTs) replaced PFOS in FSBFs when 3M ceased PFOS production, but the situation is not that simple. The other raw material suppliers for foam manufacturers were actually selling fluorotelomers for this purpose well before the planned PFOS production shutdown. Today, several classes of zwitterionic, cationic, and anionic fluorotelomers are used in FSBF formulations, with six perfluorinated carbons (C6) or a mixture of six and eight perfluorinated carbons (C6/C8) (Seow, 2013). Nevertheless, C8-C20- γ - ω -perfluorotelomer thiols with acrylamide (CAS number 70969-47-0) was still in use in 2013, although its degradation products may include long-chain PFASs (Nordern, 2013; Seow, 2013). One of the drawbacks of short-chain fluorotelomers is that higher concentrations of fluorinated surfactants are needed to achieve acceptable efficiency for FSBF formulations (Nordern, 2013). Manufacturers consider the chemical structure of the fluorinated surfactants used in commercial FSBFs as trade secrets and surrogate parameter methods (oxidative conversion of PFCA precursors or total organofluorine content) revealed that a significant portion of fluorinated surfactants was not identified in some of the foam concentrates analyzed (Houtz et al., 2013; Weiner et al., 2013). However, technical knowledge has greatly improved in recent years (Backe et al., 2013; D'Agostino and Mabury, 2014; Houtz et al., 2013; Moe et al., 2012; Place and Field, 2012; Weiner et al., 2013), and the identified fluorotelomers are presented in Table S1.

Fluorinated surfactants were present at a level of 1.5–6.5% by weight in a foam concentrate manufactured by 3M (Moody and Field, 2000). In recent studies, individual PFAS concentrations ranged from low $\mu\text{g/L}$ levels to g/L levels (Backe et al., 2013; Houtz et al., 2013; KEMI, 2015; Weiner et al., 2013). The foam is made by

first mixing foam concentrate with water to create a foam solution (dilution with 94%, 97% or 99% water according to specifications). This aqueous solution is then combined with air using aspirating nozzles at the point of use (Pabon and Corpart, 2002; Scheffey and Hanauska, 2002).

Besides fluorinated surfactants, FSBFs also contain other ingredients such as solvents (2-butoxyethanol, 2-(2-butoxyethoxy) ethanol, 1,2-ethanediol, triethanolamine, etc.), hydrocarbon surfactants (sodium alkyl sulfate, alkyl glucoside, alkyl amidobetaine, etc.), and additives (tolyltriazole, polysaccharide, etc.) (Harding-Marjanovic et al., 2015; Laitinen et al., 2014; Moody and Field, 2000; Pabon and Corpart, 2002).

The use of these foams for incidents and exercises leads to direct emissions of PFASs into the environment and contamination of surface water (Ahrens et al., 2015; Arias et al., 2014; Filipovic et al., 2015; SFT, 2008; Taniyasu et al., 2015), groundwater (Backe et al., 2013; Filipovic et al., 2015; Houtz et al., 2013; Moody and Field, 1999; Schultz et al., 2004; SFT, 2008; Weiss et al., 2012), seepage water (Kärman et al., 2011), wastewater (Houtz et al., 2016), sediment (Ahrens et al., 2015; Kärman et al., 2011), biota (Ahrens et al., 2015; Awad et al., 2011; Gewurtz et al., 2014; Kärman et al., 2011; Oakes et al., 2010; SFT, 2008) and soil (Filipovic et al., 2015; Houtz et al., 2013; Kärman et al., 2011; Moe et al., 2012; SFT, 2008; Taniyasu et al., 2015; Weber et al., 2010). Accidental releases at airports also contribute to environmental contamination (Awad et al., 2011; Kwadijk et al., 2014; Moody et al., 2002). From 1965 to 1974, it was estimated that 50–100 tons of PFCAs were released into soil and water from the use of FSBFs all over the world (Prevedouros et al., 2006). For PFOS derivatives, these emissions were estimated to be 9150 tons over the 1970–2002 period (Paul et al., 2009). Once released into the environment, fluorotelomers and PFSA derivatives are transformed into perfluoroalkyl acids (PFAAs), which have been detected at high concentrations (Table S2). However, other fluorinated metabolites—often overlooked—should also be taken into consideration when assessing the overall impact of these releases (Harding-Marjanovic et al., 2015; Moe et al., 2012; Place and Field, 2012). Since their complete quantitation is impossible due to the lack of standards and the variety of potential metabolites (Mejia-Avendaño et al., 2016), the use of surrogate parameter methods could be very helpful for investigating the fate and behavior of fluorinated surfactants in the environment (Harding-Marjanovic et al., 2015; Houtz et al., 2016; Taniyasu et al., 2015; Willach et al., 2016).

In the present study, the environmental impacts of FSBF releases were evaluated through the collection of several surface water, groundwater and sediment samples in the vicinity of four sites where these foams had or are still being heavily used. In addition to the quantification of 32 PFASs, the total concentration of perfluoroalkyl acid (PFAA) precursors was also indirectly measured by the use of an oxidative conversion method (Houtz and Sedlak, 2012). Moreover, nine foam concentrates were analyzed to identify the PFASs which are added to these formulations. The results were used to assess the implications of FSBF applications in the long-term contamination of aquatic environments and to determine the formulations of some FSBFs that are in current use.

2. Material and methods

2.1. Firefighting foam concentrates

Nine firefighting foam concentrates were provided by a professional user. Five concentrates were AR-AFFFPs, two were AR-AFFFs, one was a FFFP and one was fluorine-free (Table S3). These concentrates were manufactured after 2002 by four different manufacturers (hereafter referred to as W, X, Y and Z). The

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