



Deep seepage of per- and polyfluoroalkyl substances through the soil of a firefighter training site and subsequent groundwater contamination

Xavier Dauchy*, Virginie Boiteux, Adeline Colin, Jessica Hémard, Cristina Bach, Christophe Rosin, Jean-François Munoz

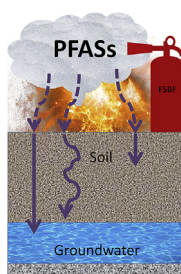
ANSES, Nancy Laboratory for Hydrology, Water Chemistry Department, 40 Rue Lionnois, 54000 Nancy, France



HIGHLIGHTS

- PFAS measurement in groundwater and soil cores impacted by firefighter training.
- Deep seepage (–15 m) of many PFASs, including fluorotelomers, through soil.
- Many monitoring wells and one drinking water resource were contaminated.
- Many classes of key fluorinated ingredients of foams were detected.
- Some fluorotelomers reached the groundwater despite overlying clay.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 May 2018
Received in revised form
25 September 2018
Accepted 1 October 2018
Available online 2 October 2018

Handling Editor: Myrto Petreas

Keywords:

Firefighting foam
Per- and polyfluoroalkyl substance (PFAS)
Water contamination
Total oxidizable precursor method
Soil contamination
Seepage through soil

ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) are utilized in specific firefighting foams. The objectives of this study were i) to map PFAS distribution in the soil and groundwater of a firefighter training site active for more than 3 decades, ii) to locate the main points of entry of PFASs into the aquifer and iii) to identify which PFASs seeped most deeply into the soil. A total of 44 soil cores and 17 groundwater samples were collected. Perfluorooctane sulfonate (PFOS), 6:2 fluorotelomer sulfonic acid (6:2 FTSA) and 6:2 Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) were the most predominant PFASs in surface soil. The highest total PFAS concentrations (up to 357 $\mu\text{g/g}$) were measured in two areas. Both areas were considered as potential points of entry of PFASs into the aquifer since PFASs were detected in soil 15 m below the surface, despite the presence of clay layers. The highest total PFAS concentrations were recorded in the monitoring wells located in the perimeter of the firefighter training site and in the spring located downgradient in the direction of groundwater flow. They ranged from 300 to 8300 ng/L. The fluorotelomer 6:2 FTAB was quantified in 6 monitoring wells, suggesting that this FT can reach a water table 20 m below the ground's surface.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are powerful surfactants that have been produced since the 1950s (Buck et al., 2011; Prevedouros et al., 2006). Some of these substances are key

* Corresponding author.

E-mail address: xavier.dauchy@anses.fr (X. Dauchy).

constituents of fluorosurfactant-based foams (FSBFs) as they decrease the surface tension of water and form a film over the fuel surface (Buck et al., 2011; Kissa, 2001). These foams have been used since the 1960s to extinguish fuel-based fires (i.e. gasoline and kerosene). The widespread use of FSBFs during firefighter training exercises (at civilian airports, military bases or oil refineries, for example) or during accidental fires (e.g. oil storage tank fires or aircraft crashes) leads to PFAS contamination of soil, sediment, surface water, groundwater and biota (Backe et al., 2013; Bräunig et al., 2017; Filipovic et al., 2015; Houtz et al., 2013; Kärrman et al., 2011; Lanza et al., 2017; Munoz et al., 2017; Weber et al., 2017). The chemical structure of the fluorinated surfactants used in commercial FSBFs is the manufacturer's proprietary information and is therefore not usually disclosed. However, technical knowledge has greatly improved in recent years and several classes of PFASs present in FSBFs have been identified (Backe et al., 2013; Barzen-Hanson et al., 2017b; D'Agostino and Mabury, 2014; Place and Field, 2012; Weiner et al., 2013). Thus, different perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs) and fluorotelomers (FTs) have been identified and quantified in FSBFs. PFCAs and PFSAs are highly persistent in the environment (Buck et al., 2011), and those with a long perfluoroalkyl chain (with 7 or more perfluorinated carbon atoms) tend to be highly bioaccumulative (Krafft and Riess, 2015). Concerns about their toxicity have led several countries, including the USA (US-EPA, 2016) and Germany (FEA, 2011), to issue guidance values for perfluorooctane sulfonic acid (PFOS) and perfluorooctane carboxylic acid (PFOA). However, environmental samples from a contaminated area often contain a mixture of many PFASs.

For FSBF-impacted sites, the interpretation of environmental monitoring results proves to be a challenging task. When a PFAS is detected in an environmental sample, it is difficult to know whether it originated directly from the application of FSBF or whether it is a transformation product of a precursor, with the exception of parent fluorotelomers with a high molecular weight, such as fluorotelomer sulfonamido betaines (FTABs), fluorotelomer thioether amido sulfonates (FTSAs) or perfluoroalkyl sulfonamido amines (PFnSAs).

For instance, PFOS and perfluorohexane sulfonic acid (PFHxS) are intentionally-added ingredients of FSBFs (Field et al., 2003; Houtz et al., 2013; Laitinen et al., 2014; Place and Field, 2012), but they can also be transformation products of PFASs used in FSBFs such as PFnSAs (Mejia-Avenidaño et al., 2016) or other PFSA-based molecules (Kishi and Arai, 2008). Likewise, fluorotelomer sulfonic acids (FTSAs) are present in some FSBF formulations (Backe et al., 2013; Houtz et al., 2013; Schultz et al., 2004) at concentrations above 10 mg/kg, but they are also transformation products of FTSAs (Harding-Marjanovic et al., 2015; Weiner et al., 2013) or FTABs (D'Agostino and Mabury, 2017). Finally, PFCAs were used as a component in FSBFs in the early 1970s (Prevedouros et al., 2006) and were detected as by-products in some 3M formulations manufactured with the electrochemical fluorination method (Backe et al., 2013; Houtz et al., 2013; Weiner et al., 2013), but they are also end-stage biotransformation products of fluorotelomers used in FSBFs (D'Agostino and Mabury, 2017; Harding-Marjanovic et al., 2015; Zhang et al., 2016).

The objectives of this study were i) to map PFAS distribution in the soil and groundwater of a firefighter training site where FSBFs have been used intensively for more than 3 decades, ii) to locate the main points of entry of PFASs into the aquifer and iii) to identify which PFASs seeped most deeply into the soil. To address these questions, 44 soil cores and 17 groundwater samples were collected over 2 sampling campaigns and analyzed so as to measure first of all those PFASs able to be measured directly. In addition, the total

oxidizable precursor assay (Houtz and Sedlak, 2012) was conducted on selected groundwater samples to highlight the presence of unidentified PFAA precursors. Finally, a suspected-target screening method based on recently identified PFASs in FSBFs (Barzen-Hanson et al., 2017b) was applied to selected soil and groundwater samples. Due to the lack of standards, the PFASs on the "suspected target" list were not quantified, but this screening step provided information on their occurrence and fate in soil. To the best of our knowledge, this study provides the first evidence of the seepage and soil mobility of PFASs down to 15 m below the ground.

2. Materials and methods

2.1. Site information

Groundwater samples and soil cores were collected from a site covering a fenced area of 1.7 square kilometers where FSBFs have been used intensively (Fig. 1). From 1969 to 1984, this site was an oil refinery. The exact location of the training area, the frequency of training sessions and the history of firefighting training activities are unknown within that period. From 1987 to date, it has been a large training area for firefighters. Originally, the exercises were carried out directly on the soil. From the 1990s onward, some of the exercise areas were covered with concrete. Between 2006 and 2015, 0.4 m³–0.8 m³ of FBSF per week was used for the exercises (0.6 m³ on average), which is low in comparison with US military bases, where an average of 3 m³ may be used every week (Moody and Field, 2000). Records of the exact makeup of FSBF formulations used onsite are unavailable, as are the annual quantities used between 1987 and 2006. It is quite likely that several kinds of FBSFs manufactured by different companies were used onsite, including FBSFs containing PFSA precursors as the main ingredient. Under the site, there is an unconfined water table ranging from 20 m to 40 m deep. Overall, the site's soil is composed of sand, silt and clays for the first 10 m, and rests on alternating marl and limestone formations of varying thickness dating from the Lutetian and Bartonian periods. The unconfined water table is located in a 10-m thick layer of sand over clays from the Sparnacian period. The soil above the water table is considered as permeable/medium-permeable by geologists who studied the site. In November 2014, some PFASs were measured in groundwater samples and a well supplying drinking water was closed on the basis of the precautionary principle (Boiteux et al., 2016; Dauchy et al., 2017).

2.2. Groundwater and soil collection

Two sampling campaigns were carried out in 6 selected areas (Fig. 1 and S1). The aim of the first one (June 2015) was to identify the most contaminated areas. Thirty soil cores were collected in the vicinity of 5 areas suspected to be affected by firefighting activities. The depth of soil cores ranged from 2 m to 4 m, and composite soil samples were collected every 25 cm in the topmost meter and then every 50 cm. Additionally, 13 water samples were collected from 9 monitoring wells and 4 springs. The aim of the second sampling campaign (October 2016) was to probe more deeply into the most contaminated areas detected during the first campaign and to investigate an overlooked area (#6 on Fig. S1). Fourteen soil cores were collected from between 4 m and 15 m deep. The thickness of composite soil samples ranged from 25 cm to 100 cm according to the studied area. Four water samples were also collected from 4 monitoring wells, including a new well that was drilled before the second sampling campaign (MW-12). Detailed information on all the sampling points (collection, location, and geological cross-section for every soil core) is given in the supplementary material (Figs. S2–S14).

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