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Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish

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HIGHLIGHTS

- PFOS in soil, surface and ground water is attributed to historical use of AFFF.
- PFOS and PFOA in soil cores remained in high concentrations >30 years after AFFF usage.
- PFAAs leaching from contaminated soil can be a source of PFAAs in ground water.
- PFOS in fish muscle from Lake Bysjön are among highest previously reported.

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ABSTRACT

Historical usage of aqueous film forming foams (AFFFs) at military airports is a potential source of perfluoroalkyl acids (PFAAs) to the nearby environment. In this study, the distribution of perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) in soil, groundwater, surface water, tap water well, and fish muscle was investigated at a closed down military airfield (F18) and its surroundings in Stockholm, Sweden. The presence of PFOS at AFFF training sites was inventoried.

One major finding of the study is that a former airfield, abandoned since 1994, may still be a point source of PFAAs to nearby recipients. PFOS and PFOA were ubiquitous in the soil samples at former AFFF training sites with concentrations ranging from 2.18 to 8520 ng g^{-1} dry weight and <0.12–287 ng g^{-1} dry weight respectively. The sum of PFAAs in the groundwater and surface waters ranged from 738 to 51 000 ng L^{-1} and <MDL to 79.0 ng L^{-1}, respectively. PFOS in European perch ranged from 76.5 to 370 ng g^{-1} wet weight muscle tissue which is among the highest previously reported worldwide. Our results provide evidence that the historical use of AFFF at the site have contaminated an aquifer (7500 m^3 d^{-1}), that will require constant PFAA purification before being used for drinking water production. Despite the fact that the water turnover time in the investigated recipients (of 4–6 months) suggest a depletion of PFAA-contaminants over a quarter of a decade, abandoned airfields may still pose an environmental and human health concern.

1. Introduction

Perfluoroalkyl acids (PFAAs) have been produced since 1950s (Prevedouros et al., 2006). The unique amphiphilic properties of PFAAs makes them applicable in several commercial and industrial applications such as food packaging material and aqueous film forming foams (AFFFs) (Kissa, 2001). Direct and diffuse sources of PFAAs to the environment combined with precursor degradation, (Ellis et al., 2004) and exceptional stability results in ubiquitous presence of PFAAs in the environment (Ahrens et al., 2010). Of these perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have shown to bioaccumulate and have toxic potential to aquatic and mammalian species (Lau et al., 2007). Extensive

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usage of AFFFs have been suggested to be one important point source of PFAAs to lakes within urban areas (Ahrens et al., 2014).

AFFFs were introduced in the 1960s when the 3M Company together with the United States Navy developed AFFFs to extinguish hydrocarbon-fuel fires (Schultz et al., 2004). Polyfluorinated substances and PFAAs are some of the main compounds in the AFFF formulas. Adding PFAAs to AFFFs results in lowering the surface tension, and hence more efficient spreading of AFFFs on lighter fuels and water, increasing the fire control efficiency compared to AFFFs based on non-fluorinated surfactants (Kishi and Arai, 2008). The deployment of AFFFs for emergency and training purposes and their repeated usage, particularly at military bases, airports, oil rigs and municipal fire departments has resulted in direct releases to the environment (Moody and Field, 2000). Historically, effluents from AFFF fire-fighting training activities were neither collected in basins nor pre-treated prior to discharge to waste water treatment plants or to the environment. Such releases may be responsible for the presence of PFAAs in the vicinity of firefighting training sites.

As AFFFs are predominantly released in liquid form, this increases the potential for the PFAAs to enter the aqueous environment. Several studies have pointed out usage of AFFF as a possible source of PFAAs to the groundwater (Moody and Field, 1999; Moody et al., 2003; Schultz et al., 2004; Houtz et al., 2013), drinking water (Weiß et al., 2012), surface water (de Solla et al., 2012; Ahrens et al., 2014) and biota (Oakes et al., 2010; Gewurtz et al., 2014). One of the first studies to address the issues with leakage of AFFFs and PFAAs contamination of ground water at a military airfield was done by Moody and Field (1999). PFOS is the most predominant PFAA at AFFF contaminated sites and has been detected in >600 ng L^{-1} concentrations in surface water and in hundreds of ng g^{-1} in fish homogenate (Awad et al., 2011). However; there is a lack of knowledge regarding multimedia distribution of PFAAs from the contaminated sites to the surrounding environment.

The objective of this study was to examine the transport and fate of PFAAs in soil, water and fish at the former military airport F18 in Stockholm, Sweden. The specific objectives were to identify all potential sites where AFFFs had been used, historically. Samples of surface soil, ground water, surface water and fish muscle tissue were collected and analysed. In addition soil cores were collected in order to investigate migration of PFAAs at AFFF practicing sites. This study may be used as a basis for human risk analysis of PFAAs at point sources.

2. Material and methods

2.1. Site description

The air force base F18 in Tullinge Riksten, 19 km south of Stockholm City center (Sweden) see Fig. 1, was established in 1946 and was formally demobilized in 1986. The area remained as an air force school for combat command and air surveillance until 1994. The air force base was intensively used during 1950–1961 when the air force was transformed from using propeller propulsed fighters into a jet propulsed air force. In 1996 the area was sold to a land developer who subsequently has been transforming the area into a municipal area that, when fully developed, will host 10 000 inhabitants. The area spans a circumference of approximately 10 km and has an area of ca 3.4 km^2, see Fig. 1B. The hydrogeology on the site have shown that the ground water flow is directed from the military airfield towards Lake Tullingesjön, see Fig. 1C. On top of the ground water aquifer is a thick layer (30 m) of glacial debris and gravel. The ground water is used for tap water production and in 2011 approximately 16 500 inhabitants were supplied while the daily pumped volume exceeded some 7500 m^3.

2.2. Key points from interviews for selection of sampling sites

In order to reduce the area of possible interest with regard to the mapping of PFAAs-dispersion at a location that nowadays carries very little resemblance to an air force base, a set of interviews were conducted. The main information provided by the interviews regarded (a) the different locations where AFFF-foams had been used in fire-fighting exercises, (b) information on regular exercises (*duration*, *frequency*, *procedure*) using AFFF, (c) positions of the air force base where jet airplanes had crashed and/or caught fire and whereupon AFFF was used and dispersed in vast quantities, (d) where AFFF-foams had been stored, (e) procedures for handling and dilution of AFFF-formulations, (f) information on misuse and improper handling of AFFF-based sprinklers at the cave hangar system. For additional information see Electronic supplementary material (ESM) (1. Interview of participants).

In addition allocation of large soil masses were observed between the intermediate soil depot to the soil depot, these sites were assembled by the land developing company. To ensure that no "dig and dump" contamination is occurring soil samples were collected and analysed at both locations.

2.3. Sampling sites

2.3.1. Soil and soil cores

Soil samples were collected during two sampling campaigns in December 2011 and May 2012. In total 45 soil samples at depths 0–2 m were collected at five different locations, the old fire station ($n = 5$), J34 Hawker Hunter impact site ($n = 5$), Napalm training ground ($n = 15$), intermediate soil depot ($n = 10$), soil depot ($n = 10$), see Fig. 2. Soil samples were sampled using methanol-wiped shovels and buckets.

Soil cores were collected, from three sites the main firefighting training facility ($n = 6$) were sampled from 0 to 3 m, Napalm training ground ($n = 8$) and old fire station ($n = 8$) were sampled from 0 to 4 m with 0.5 m interval see Fig. 2. Soil cores were sampled using a tracked drilling rig. Prior to drilling and intermittent between different drilling depths, the drill was wiped with a methanol-soaked tissue in order to minimize cross contamination between sampling points and sampling depths.

In addition, the total mass of PFOS in the top three meters was calculated at the main firefighting training facility, Napalm training ground and the old fire station using the software ProUCL v4.0 see ESM (2 Estimation of PFOS in soil).

2.3.2. Groundwater and surface water

Ground water and tap water well samples were collected at the airfield and in the vicinity of the airport during the same time as soil samples. In total 16 ground water samples were collected in addition to 10 tap water well samples. Prior to ground water sampling, the pumps and tubing utilized was tested for leachability of PFAAs in a small tank of double-distilled ion-exchanged water. Several hours of pumping the double-distilled ion exchange water with the immersed pumps and tubing, resulted in minor additions of PFAAs to the tank water (<1 ng L^{-1}, 15 L tank). Also the oils and greases of the drilling rig was sampled and analyzed with respect to the PFAA-contents. All ground water wells were pumped dry 3–4 times prior to sampling. As for drinking water sampling in private homes, the tap was allowed to run for 1–2 min prior to sampling.

Surface waters samples including lakes and ponds were collected during two sampling campaigns in December 2011 and April 2012. In total 14 surface water grab samples were collected using a dip sampler, see Fig. 1B. All water samples were collected in 1 L high-density polypropylene (HDPE) bottles and stored at 4 °C until analysis.