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Research Paper

The effects of fluoride based fire-fighting foams on soil microbiota activity and plant growth during natural attenuation of perfluorinated compounds

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ABSTRACT

The use of fluoride based foams increases the effectiveness of fire-fighting operations, but they are also accompanied by major drawbacks regarding environmental safety of perfluorinated compounds (PFCs). The main concern with PFCs release is due to their well-known persistence and bioaccumulative potential, as they have been detected in many environmental samples. There is a significant knowledge gap on PFC toxicity to plants, even though such data could be useful towards bioremediation procedures. It is consensus that a realistic assessment of fire-fighting foam toxicity should cover as many test organisms as possible, however, few studies combine the performance of ecotoxicological tests with a detailed study of microbial communities in soil contaminated with firefighting foams. Our research evaluated the effects of natural attenuation of PFCs on the development of arugula and lettuce seeds. The effects of variable PFCs amounts were also observed in soil microbiota using the 2,6 dichlorophenol-indophenol redox dye as microbial metabolism indicator. We aimed to determine whether aqueous film forming foams toxicity increased or decreased over time in a simulated contamination scenario. We argued that the long-term biotransformation of fire-fighting foams should be taken in to account when evaluating toxicity, focusing on a time-based monitoring analysis, since potentially toxic intermediates may be formed though biodegradation. The phyto-toxicity of PFCs to lettuce and arugula was high, increasing as a function of the concentration and decreasing as a function of exposure time to the environment. However, very specific concentrations throughout biodegradation result in the formation of non-inhibiting intermediates. Therefore, variable biodegradation-dependent germination rates may be misleading on non-time-based monitoring approaches. Also, the low phyto-toxicity after 240 days does not exclude the potential for PFC bioaccumulation in plants. We also proposed that the colorimetric data modelling could also establish a novel toxicity parameter to evaluate the release impacts to soil and biota. The combined assays allowed the monitoring of PFCs during long-term exposition to plants as well as their immediate effects on the same soil microbiota.

1. Introduction

Firefighting foams have been developed for better adhesion to materials on fire, producing a continuous coating on it. Their low density allows better spreadability over the surface of burning materials, covering and isolating them from atmospheric oxygen. The suppression of oxygen and the cooling of burning materials prevent re-ignition. The use of fluorine-containing aqueous film forming foams (AFFF) has improved the firefighting effectiveness of hydrocarbon related operations (Sardqvist, 2002) aiming to ensure the promptness and safety of firefighting techniques. The AFFF advantages are clear, but they are also accompanied by major drawbacks concerning environmental safety.

Firefighting foams contain various substances to achieve proper formation of foam and grant its functional properties. Most of the foam compounds are fluorinated surfactants or hydrolyzed

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proteins, solvents and water. Commercial formulations of AFFF are complex mixtures whose main components are a solvent (typically a glycol ether), fluorinated surfactants (amphoteric or anionic partially fluorinated or perfluorinated), and surfactant-based hydrocarbons. Fluorinated surfactants in AFFF contribute to its performance when extinguishing fires (Kissa, 1994; Alm and Stern, 1992; Falk, 1978). The presence of fluorine contributes to the rigidity of perfluorocarbon chains (Key et al., 1997). The fluoro-carbon bond is strongly polarized. Fluorination also reinforces C—C adjacent bonds (Hudlicky and Pavlath, 1995). Therefore, perfluorinated surfactants are more thermally stable than their corresponding hydrocarbon analogs. In particular, perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs), both found in AFFF, are among the most thermally stable perfluorinated compound (PFC) groups. In addition to thermal stability, perfluorinated surfactants are stable to acids, bases, oxidizers and reducers. This stability allows fluorinated compounds to remain intact in environments where hydrocarbon surfactants are degraded (Kissa, 1994).

The main concern with AFFF release is due to PFCs persistence and their bioaccumulative potential. They have been detected in many environmental samples, including air, surface water (Murakami et al., 2008; Kim and Kannan, 2007), waste waters (Sinclair and Kannan, 2006), soil (Higgins et al., 2005) and groundwater (Schultz et al., 2004). PFCs were also found accumulating in biota, including mammals (Giesy and Kannan, 2002) and humans (Hölzer et al., 2008). The PFCAs, PFSAs and their potential precursors have attracted attention as global contaminants (Buck et al., 2011). PFCAs and long chain PFSAs are described as very problematic because they are highly persistent (Frömel and Knepper, 2010), bioaccumulative and found scattered almost universally in abiotic environments (Rayne and Forest, 2009), in biota (Giesy and Kannan, 2001), food (Clarke and Smith, 2011) and humans (Vestergren and Cousins, 2009). As a result, many firefighting foams based on PFCs had their production restricted and were listed as substances of very high concern in European Regulation of Chemicals (ECHA, 2013).

The AFFFs are predominantly released in the form of liquid foam, which increases the potential of PFAS to penetrate in aquatic environments. The PFC inflow to the medium may occur via four routes: (i) release of volatile PFCs into the atmosphere (Dinglasan-Panlilio and Mabury, 2006), which is oxidized photochemically (Ellis et al., 2004) and back to the water cycle by precipitation; (ii) discharge to wastewater treatment plants (Yu et al., 2009); (iii) discharge of urban runoff contaminated by diffuse sources (Houtz and Sedlak, 2012; Zushi and Masunaga, 2009), and (iv) the infiltration of waste and spills in groundwater (Moody and Field, 2000; Moody et al., 2003). Even though the PFC abiotic routes have been continuously investigated, there is still a lack of knowledge about the PFCs from the toxicological standpoint in many organisms.

Toxicity data can be used to better remediate AFFF contaminated areas. Toxicity tests are based on determining the potential impact of pollutants towards biota in a set environment (Hagner et al., 2010). Thus, ecotoxicological datasets have long been used with relative success as an additional tool for monitoring the efficiency of soil bioremediation, making it essential to assess environmental hazards in contamination scenarios (Lladó et al., 2012; Sheppard et al., 2011). However, few studies combine the performance of ecotoxicological tests with a detailed study of microbial communities in soil contaminated with firefighting foams.

It is consensus that a realistic assessment of AFFF toxicity should cover as many test organisms as possible. Phyto-toxicity tests with AFFF sources are scarce in current the literature. We also argue that the biotransformation of AFFF compounds should be taken in to account when evaluating long-term toxicity, as potentially toxic intermediates may be formed. Our research evaluated the effects of natural attenuation of AFFF on the development of plants. We aimed to determine whether AFFF toxicity increases or decrease over time in a simulated soil contamination scenario. Unlike most studies found in the literature, which monitor AFFF original formulation or persistent final biotransformation products, we designed intermediate toxicity evaluation points. Changes that affected the development of vegetable tissues provided an overall assessment of PFCs environmental safety. Moreover, we aimed to propose a novel toxicity classification towards environmentally safe release of pollutants using a colorimetric approach. A redox indicator (2,6 dichlorophenol-indophenol) usually associated with biodegradation studies was repurposed by our research group to evaluate soil microbiota response to various concentrations of AFFF.

2. Material and methods

2.1. Soil samples

Soil samples were acquired from the Biosciences Institute Experimental Garden at the Sao Paulo State University in Rio Claro, SP, Brazil (22°43′24.2″S 47°08′00.3″W). The area has a petroleum contamination background that is analogous to oil industry sites affected by hydrocarbon fires. The sampling area has been exclusively used for experiments with gasoline, diesel, kerosene and other petroleum hydrocarbons over the past 8 years.

2.2. Toxicity assessment of AFFF dilutions

Various dilutions of AFFF samples were prepared from stock AFFF solution. In this first group of experiments no soil was added to the assays. We evaluated pure AFFF effects on plants germination, wherein the concentration of perfluorinated compounds was 195 g L^{-1}. Dilutions were then made to match 3% and 1% concentrations, yielding 97.5 and 19.5 g L^{-1} of PFCs. Both dilutions are also available from firefighting foam distributors. The solutions were then directly inserted into toxicity bioassays for the germination and development of seeds.

2.3. Toxicity throughout biodegradation

A set of experiments on toxicity was performed to evaluate AFFF toxicity at different concentrations through natural attenuation. The soil matrix was designed to simulate widespread PFC contamination scenarios with AFFF. The biodegradation environment was set up through a simulated soil contamination within a plastic bag filled with 3 kg of soil and 0.1x, 1x and 10x m/v AFFF (Table 1). The container had small holes with approximately 1 mm diameter, spaced 1 cm each, to promote the exchange of microorganisms between the inner soil and the external environment. The recipient was buried 5 cm from the surface. We used the retail 6% AFFF (Sintex S1371/11) formulation, commercially available and commonly applied to petroleum fires in Brazil. Its formulation contains

Table 1
Phyto-toxicity bioassays.

Sample ID	Components	AFFF Concentration	Biodegradation time
C0	Soil	–	0 days
C60	Soil	–	60 days
C120	Soil	–	120 days
C180	Soil	–	180 days
C240	Soil	–	240 days
F0	Soil + AFFF	0.1x, 1x and 10 x m/v	0 days
F60	Soil + AFFF	0.1x, 1x and 10 x m/v	60 days
F120	Soil + AFFF	0.1x, 1x and 10 x m/v	120 days
F180	Soil + AFFF	0.1x, 1x and 10 x m/v	180 days
F240	Soil + AFFF	0.1x, 1x and 10 x m/v	240 days