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Biodegradability of fluorinated fire-fighting foams in water

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HIGHLIGHTS

- Three fluorinated fire-fighting foams met the 28-day "ready biodegradability" criteria.
- Fluoride released during biodegradation was 1–2 orders of magnitude lower than estimated.
- Chemical oxygen demand (COD) did not accurately quantify fluorinated organics.
- Perfluorinated organics from foams were found to have high resistance to oxidation.

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ABSTRACT

Fluorinated fire-fighting foams may be released into the environment during fire-fighting activities, raising concerns due to the potential environmental and health impacts for some fluorinated organics. The current study investigated (1) the biodegradability of three fluorinated fire-fighting foams, and (2) the applicability of current standard measures used to assess biodegradability of fluorinated fire-fighting foams.

The biodegradability of three fluorinated fire-fighting foams was evaluated using a 28-day dissolved organic carbon (DOC) Die-Away Test. It was found that all three materials, diluted in water, achieved 77–96% biodegradability, meeting the criteria for "ready biodegradability". Defluorination of the fluorinated organics in the foam during biodegradation was measured using ion chromatography. It was found that the fluorine liberated was 1–2 orders of magnitude less than the estimated initial amount, indicating incomplete degradation of fluorinated organics, and incomplete C—F bond breakage.

Published biodegradability data may utilize biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) metrics to quantify organics. COD and TOC of four fluorinated compounds were measured and compared to the calculated carbon content or theoretical oxygen demand. It was found that the standard dichromate-based COD test did not provide an accurate measure of fluorinated organic content. Thus published biodegradability data using COD for fluorinated organics quantification must be critically evaluated for validity. The TOC measurements correlated to an average of 91% of carbon content for the four fluorinated test substances, and TOC is recommended for use as an analytical parameter in fluorinated organics biodegradability tests.

1. Introduction

Aqueous film forming foams (AFFFs) are used to extinguish fires where flammable, volatile liquids are the fuel source (Class B fires). AFFFs consist of an air–liquid mixture of foaming agents comprised of constituents with low surface tension. The low density foam layer smothers the flame to isolate the oxygen supply, separating the fuel and the fire, cooling the fuel, and suppressing flammable vapors (IFSTA, 1994). Alcohol-resistant and protein based foams are also available.

Fluorinated surfactants provide performance superior to hydrocarbon surfactants (Kissa, 1994; Moody and Field, 2000) in fire-fighting foams. Typical fluorinated surfactants include perfluorinated acid and salt PFOA and PFOS (perfluorooctanoic acid, perfluorooctane sulfonate). The high carbon–fluorine bond strength contributes to this performance in foams. Specifically, the single bond formed between carbon and fluorine is the strongest of any known bond, and bond strength increases with the degree of fluorination in the molecule (Shepard and Sharts, 1969). PFOA, PFOS, and other long-chain perfluorinated

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compounds have been tracked in the global environment and have been found at detectable levels in numerous organisms, including humans (Lau et al., 2007; Post et al., 2012; Vierke et al., 2012). These and certain related compounds have proven to be persistent in the environment and bioaccumulative (OECD, 2002; U.S. Department of Health and Human Services, 2009; EPA, 2009).

The electrochemical fluorination manufacturing process produces fully fluorinated compounds such as PFOA and PFOS with linear or branched chains. An alternative process, telomerization, produces linear fluoroalkyl chains consisting of a fluorinated portion attached to an ethyl group followed by a non-fluorinated end-group (Moody and Field, 2000). Chain lengths and functional group identities vary. Compounds produced through telomerization biodegrade more readily than perfluorinated compounds while still being able to offer the surfactant properties desired in AFFFs (Cortina and Korzeniowski, 2008). Identities of surfactants in foam formulations are proprietary, however some components and degradation products have been identified (Schultz et al., 2004; Place and Field, 2012; Backe et al., 2013; D'Agostino and Mabury, 2014). Biotransformation studies of some fluorotelomers including a fluorotelomer sulfonate specifically identified in AFFFs demonstrate that one or more CF_2 groups may be sequentially removed by wastewater treatment plant microbes (Wang et al., 2005; Weiner et al., 2013). In another study, biodegradation of the perfluorinated portion of a fire fighting foam fluorotelomer did not occur (Moe et al., 2012). Perfluorocarboxylates of varying chain length are among the per- and poly-fluorinated terminal byproducts in multiple studies, and these are microbially inert (Parsons et al., 2008). In many currently manufactured foams, a combination of fluorotelomer surfactants and hydrocarbon surfactants are used which is able to reduce fluorine content by 30–60% (Cortina and Korzeniowski, 2008).

Foam biodegradability is an important consideration as these products may be released into natural ecosystems where they may accumulate over time if not degraded by the microorganisms present in natural systems. Tests to evaluate biodegradability monitor carbon dioxide produced during bacterial digestion of a sample, reduction in organic carbon content of the solution, or oxygen uptake under aerobic conditions. The Organization for Economic Cooperation and Development published guidelines for six tests used to screen chemicals for "ready biodegradability" which meet 60–70% organic carbon reduction, CO_2 production, or O_2 consumption (OECD, 1992). Pass levels must be met within a 10-day window within the 28-day test, beginning when biodegradation has reached 10%. Similar guidelines exist in individual countries, including those published by the U.S. EPA.

The National Fire Protection Association (NFPA) has also published biodegradability recommendations and reference information relevant to foams in Standards 11, 1150, 18, and 18A (NFPA, 2009a,b, 2010a,b). It is recommended that foams selected for use on wildland and structural fires (Class A fires), as well as wetting agents which include foam concentrates, reach 60% biodegradability within 28–42 days when using the CO_2 evolution test. Class B AFFFs meeting U.S. military specifications must achieve 65% biodegradability based on a ratio of the 20-day biochemical oxygen demand (BOD) to chemical oxygen demand (COD) (U.S. Department of Defense, 1994).

These biodegradability values are believed to be quite stringent since the additional 30–40% of carbon remaining is understood to be either converted to biomass or mineralized to carbon dioxide soon after the testing period ends. However, since the high strength of carbon–fluorine bonds is expected to render fluorinated foams either non-amenable or minimally amenable to biodegradation (producing terminal byproducts which remain highly fluorinated), the low concentrations of fluorinated constituents used in foams are likely to remain in solution while overall biodegradability testing reflects degradation of hydrocarbon surfactants, solvents, freeze point depressants, and other foam ingredients. Additionally, biodegradability calculations relying on a comparison of observed BOD or carbon dioxide formation as a percentage of the overall measured COD or TOC may be inaccurate if COD or TOC tests are unable to break C—F bonds and produce falsely low COD or TOC measures, i.e. falsely high biodegradation values result. Recent biodegradability studies of fire-fighting foam (Tureková and Balog, 2010; Zhang et al., 2012; Król et al., 2012), and published manufacturers' literature (Chemguard Inc., 2010, 2011a–c; National Foam, 2013a–e; Angus Fire, 2013a–e) have reported large variability in biodegradation, from less than 1% up to 127%. This wide range of reported biodegradability indicates a need for further testing and a critical evaluation of the suitability of test methods themselves. Objectives of this study were to: (1) quantify biodegradability of fire-fighting foams using a standard OECD test, (2) quantify defluorination during biodegradation of fire-fighting foams due to C—F bond breakage, and (3) evaluate the appropriateness of TOC and COD analysis for quantifying organic content in aqueous foam solutions containing fluorinated compounds.

2. Materials and methods

2.1. Chemicals

Pentadecafluorooctanoic acid (PFOA, 96%), heptadeca fluorooctanesulfonic acid (PFOS, 40% in water), ethyl trifluoroacetate (99%), 2,2,3,3,3-pentafluoro-1-propanol (97%), 2,2,2-trifluoroethyl perfluorobutyl sulfonate (95%), and 1H,1H,2H,2H,-perfluoro-1-decanol (8:2 fluorotelomer alcohol, 97%) were supplied by Sigma Aldrich (St. Louis, Missouri). Fire-fighting foam concentrates were supplied by Ansul (Marinette, Wisconsin) which included: Ansulite 3% AFFF (AFC-3A) (product code 1010-2-016 Ana), Ansulite ARC 3×6 alcohol-resistant AFFF (AR-AFFF) (1011-2-032 ANa), and Ansul 3% Fluoroprotein (FP) Foam (1050-3-001 SBg). The recommended foam proportioning is 3% in water for AFFF and FP, and either 3% or 6% for AR-AFFF. Reagent water was prepared using a Thermo Scientific Barnstead Nanopure Life Science UV/UF system with TOC analyzer, for which effluent TOC was $\leqslant 5\ \mu g\ L^{-1}$.

Aqueous solutions of $100\ mg\ L^{-1}$ fluorinated organic samples were used for most tests. Ansul foam concentrates corresponded to concentrations of approximately 30 000–34 500 $mg\ L^{-1}$ of foam concentrate in water for a 3% solution applied to fires. The $100\ mg\ L^{-1}$ test samples were more than 300 times diluted from the 3% solution applied to fires – this replicated applied foam solutions diluted by water (in runoff, infiltration, etc.).

Additional details of materials and methods used for this work are described in Bourgeois (2014).

2.2. COD, TOC, and fluoride analysis

Chemical oxygen demand (COD) was measured with a dichromate oxidation technique using Bioscience, Inc. (Allentown, PA) low-range (5–150 mg COD L^{-1}) Accu-Test vials which contained premixed dichromate reagents consistent with Standard Methods for the Examination of Water and Wastewater Method 5220. Using a Cary WinUV spectrophotometer, light absorbance at 440 nm was correlated to COD with a potassium hydrogen phthalate (KHP, E.M. Science, Cherry Hill, NJ) standard curve.

A Shimadzu TOC-5000A Analyzer was used for total organic carbon (TOC) analysis to quantify non-purgeable organic carbon. A calibration curve using KHP standards was created prior to each round of sample measurement. Samples (10–20 mL) were acidified