Characterization of the Fate and Biotransformation of Fluorochemicals in AFFF-Contaminated Groundwater at Fire/Crash Testing Military Sites

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ABSTRACT

Background: Aqueous film forming foams (AFFF) are complex mixtures of fluorocarbon surfactants that have been an essential tool used by the DoD and others since the 1960s to extinguish fires at airports, training sites, and on ships. There are hundreds of fire/crash training areas at military sites where training fires were routinely started by igniting waste hydrocarbons or halogenated solvents and then applying AFFF, thus creating mixed-waste sites. Consequently, repeated applications of AFFF at military fire-training sites has resulted in hundreds of fluorochemical contaminated groundwater, sediment, and soil sites.

Objective: The objective of this study is to fully delineate the fluorochemicals that persist in AFFF-contaminated groundwater, sediment, and soil and evaluate their impact on priority pollutant transport and bioremediation. We intend to characterize the composition of individual fluorochemicals and their precursors in AFFF formulations and delineate the total organic fluorine concentrations of AFFF-contaminated groundwater, sediment, and soils. We will also derive field-based estimates of fluorochemical transport and retardation coefficients and establish special interactions with co-contaminant trichloroethene (TCE) in groundwater at military fire-training sites. Finally, we will establish the potential for biotransformation of fluorinated compounds in AFFF and the impact of AFFF components on TCE transformation under redox conditions that are representative of groundwater at fire-training sites.

Summary of Science or Technology: Little is known about the chemistry of AFFF beyond that it is a complex mixture of fluorochemicals and surfactants that results in the generation of persistent fluorochemicals from partially-fluorinated precursors. Our research team combines expertise in the quantitative analysis of fluorochemicals and AFFF with considerable experience assessing the fate, transport and transformation of organic contaminants in soil and groundwater. We intend to apply fast atom bombardment mass spectrometry (FAB/MS) to characterize the fluorochemical and hydrocarbon chemical classes and their respective fluorinated chain length distributions in authentic AFFF formulations and archived groundwater samples. Further, for quantification and to resolve branched from linear-chain isomers of each homolog, we will use large-volume, direct injection liquid chromatography-tandem mass spectrometry (LC-MS/MS). These methods will enable us to accurately relate the fluorochemicals detected in stockpiles and in field samples to original AFFF formulations sold on Mil Spec to the military. In order to quantify total concentrations of fluorinated compounds that serve as precursors for PFOS, PFOA and related compounds, we will develop a method that exposes samples to hydroxyl radicals as unselective oxidants prior to analysis. These methods will be applied to evaluate the biotransformation of AFFF and its breakdown products in microcosms with pristine and contaminated sediments and groundwaters.

Benefits: By developing a better understanding of the fluorochemical contaminants in AFFF and their fate and transport in the subsurface, we will enable the DoD and DoE to apply remediation approaches that greatly decrease the time and cost required to monitor and treat contaminated soil and groundwater systems.

Transition Plan: We will work with private laboratories to synthesize authentic standards of the fluorocarbon compounds. Data on newly-identified fluorochemicals associated with AFFF will be transferred to Axys Analytical Services Ltd. so that remedial site managers have access to the analytical services for monitoring and remediation. Information on fluorochemical fate and transport, and the impacts of fluorochemicals on TCE transformation will be communicated to the Naval Facilities Engineering Command Engineering Service Center in Port Hueneme, CA.