

# Quantitative Determination of Fluorotelomer Sulfonates in a Groundwater System

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## Overview

### Purpose:

To develop a LC ESI MS/MS method to simultaneously analyze perfluorinated carboxylates, sulfonates & fluorotelomerized sulfonates

### Method:

1. No sample clean-up or pre-concentration necessary
2. Analysis by LS ESI MS/MS
3. Quantitation based on calibration curves constructed from standards

### Results:

- Methodology applied to groundwater contaminated with aqueous film forming foams (AFFF)
- Fluorotelomer sulfonates (FIS) were observed at 2 out of 3 U.S. military bases, including one well with 14,600 µg/L @ Tyndall Air Force Base, FL
- AFFF may not be the source of the fluorotelomer sulfonates observed

## Methods

Groundwater + surrogate

LC ESI MS/MS



### To reduce background:

- Replace PTFE lines with PEEK
- Filter solvents with AX cartridges
- Rinse with 10% Formic/IPA overnight

### RPLC conditions:

- Waters 2690 HPLC
- Betasil C18, 2mm I.D. column
- Optima grade MeOH
- Millipore H<sub>2</sub>O w/ NH<sub>4</sub>Ac
- 30%-90% MeOH, 200 µL/min

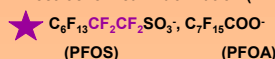
### MS conditions:

- Micromass Quattro Micro Triple Quadrupole
- Negative ESI
- Cone V ranged from 15V to 65V
- Collision E ranged from 30-45 eV

## Introduction

Fluorinated surfactants may be synthesized by one of two ways:

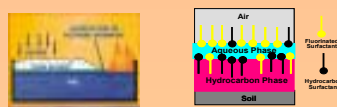
### Electrochemical Fluorination (ECF)<sup>1</sup>



Electrochemical fluorination: odd & even # carbons, branching present, all carbons fluorinated

### Aqueous Film Forming Foams (AFFF)

- Fire pose a serious threat to life & property & require immediate treatment
- AFFF developed in the 1960s by the US Navy
- AFFF blankets fuel (separates flames from fuel surface and oxygen source); fuel surface is cooled; prevents re-ignition by suppressing release of flammable vapors



### Fire-Training on US Military Bases

- Weekly-monthly training
- Flood fire pits with fuels and/or solvents
- Extinguish with 1200-3200 L of AFFF
- Mixed waste with multiple phases and components
- Disposal by infiltration or wastewater treatment

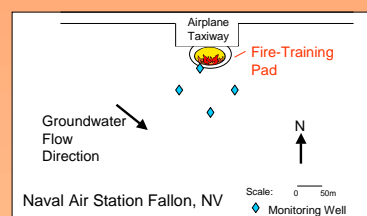
### Fluorotelomerization<sup>1</sup>



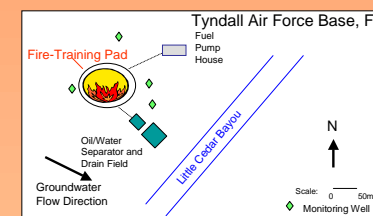
Fluorotelomerization: only even numbered carbons, no branching, C<sub>2</sub>H<sub>4</sub> spacer

## Results

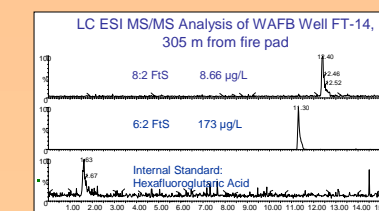
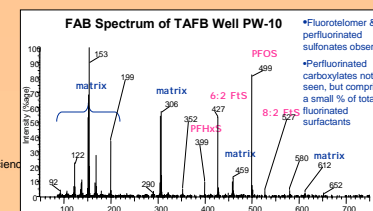
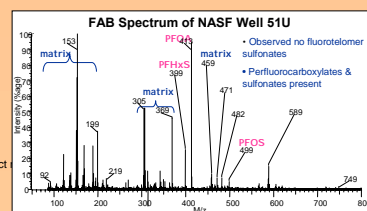
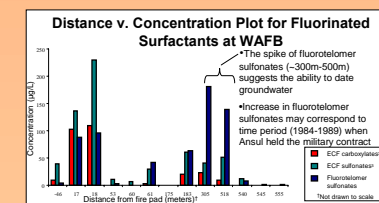
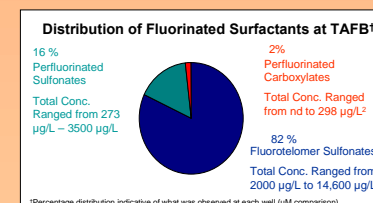
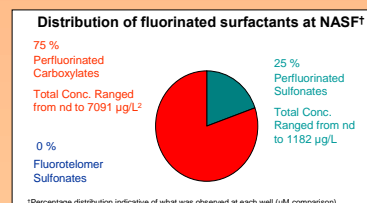
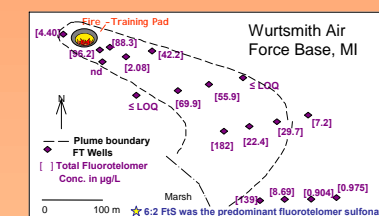
Naval Air Station (NAS)  
Fallon, NV  
Base operation: 1950's - 1988



Tyndall Air Force Base (AFB), FL  
Base operation: 1980-1992

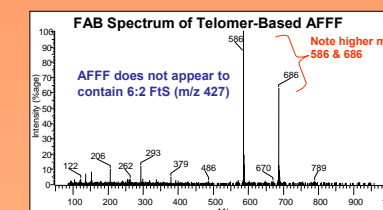


Wurtsmith Air Force Base, MI  
Base operation: 1950's - 1993

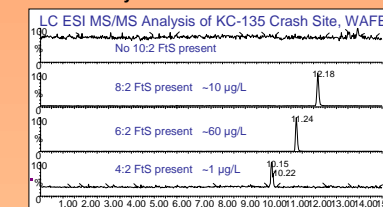


## Future Work

### Source of telomer sulfonates?



### Preliminary data:



- KC-135 Crash Site (WAFB) had a one-time application of AFFF in October 1988
- Contrasts with other fire-training sites where repeated applications occurred

## Conclusions

- LC ESI MS/MS methodology can be applied to analyze perfluorinated and fluorotelomerized surfactants
- Fluorotelomers were observed at TAFB & WAFB and their total concentrations ranged from 2000 µg/L - 14,600 µg/L and nd - 182 µg/L, respectively
- FAB/MS is a good complement to LC MS/MS for environmental analysis confirmation
- Observation at WAFB indicates potential for dating groundwater, however, retardation factors are needed for more accurate assessment

References:  
<sup>1</sup>Barke, R.E.; Smart, B.E.; Tallow, J.C. *Organofluorine Chemistry*; Plenum Press: New York, 1994.  
<sup>2</sup>Moody, C.A.; Field, J.A. *Environ. Sci. Technol.* 1998, 32, 2000.  
<sup>3</sup>Moody, C.A.; Hebert, G.N.; Strauss, S.T.; Field, J.A. *J. Environ. Monit.* 2003, 5, 341.

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