

AN ABSTRACT OF THE THESIS OF

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Title: Suspect Screening of Hydrocarbon surfactants in AFFFs and AFFF-Contaminated Groundwater by High Resolution Mass Spectrometry

Abstract approved:

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Aqueous film forming foams (AFFFs) are proprietary mixtures containing hydrocarbon surfactants and per-and polyfluoroalkyl substances (PFASs) that are used to extinguish hydrocarbon-based fuel fires. There is limited information on hydrocarbon surfactants in AFFFs and AFFF-contaminated groundwater even though they are more abundant (5-10% w/w) than PFASs (0.9-1.5% w /w) in AFFFs. Eight commercial AFFFs manufactured between 1988 and 2012 and ten AFFF-contaminated groundwaters collected from near source zones of fire-fighter training areas were analyzed for suspect hydrocarbon surfactants by liquid chromatography quadrupole time-of-flight mass spectrometry. A suspect list and a homologous series detection computational tool, enviMass, were combined to screen for suspect hydrocarbon surfactants. Nine classes of hydrocarbon surfactants were detected in AFFFs including octylphenol polyethoxylates, linear alcohol ethoxylates, ethoxylated

cocoamines, alkyl ether sulfates, alkyl amido dipropionates, linear alkyl benzene sulfonates, alkyl sulfonates, alkyl sulfates, and polyethylene glycols. Of those, six were also found in groundwater along with diethanolamides and alkyl amido betaines, which were not found in the eight archived AFFFs. This indicates that, although aerobically biodegradable, hydrocarbon surfactants likely persist in groundwater due to anaerobic aquifer conditions. To the best of our knowledge, this is the first screening for hydrocarbon surfactants in AFFFs and in AFFF-contaminated groundwater.

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Hydrocarbon surfactants in AFFFs and in AFFF-Contaminated Groundwater by
Semi-Automatic Suspect Screening High Mass Accuracy Mass Spectrometry

By

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Raymmah Aleyda García, Author

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1. Introduction

The total time from beginning of a fuel fire until conditions become fatal is three to four minutes, which means that mandatory response time of three minutes is implemented for all fire-fighting personnel.¹ Due to this time dependency, the U.S. Naval Research Laboratory developed a fire suppressant to extinguish hydrocarbon fuels as fast as possible, known as Aqueous Film Forming Foams (AFFFs).¹ The use of AFFFs began in the early 1960s^{2,3} (Hatton Jim Occurrence and behavior of per- and poly) and was used by all major airports and all U.S. Navy aircraft carriers.^{4,5} All AFFFs had to meet Military Specifications (MIL-Spec) in order to be awarded a contract and placed on a Qualified Products List (QPL).⁴ From this list, AFFFs had the potential to be sold and used, however there is no public record on contracts awarded to manufacturers or which AFFFs were used at specific sites.

AFFFs extinguish hydrocarbon based fires by creating an aqueous film that spreads across the surface.^{6,7} AFFFs are proprietary mixtures that include hydrocarbon surfactants and per- and polyfluoro alkyl substances (PFASs).^{6,8} More is known about the identity of PFASs that comprise only 0.9-1.5% w/w in AFFFs,⁹⁻¹² compared to hydrocarbon surfactants, which make 5-10% w/w of AFFFs.⁷

There are other non-military sectors that use AFFFs, such as Civil Aviation (ARFF), Oil Refineries and non-aviation Fire Departments,^{4,13} however the Military Sector is the biggest consumer of AFFFs (2,100,000 gallons).¹³ Some of the sectors, such as the Civil Aviation is heavily trafficked with civilians. According to the U.S. Bureau of Transportation Statistics, the U.S. airlines' carried an estimated 74.1 million passengers.¹⁴

In 2001, PFASs were found to be persistent and bioaccumulative in various food chains¹⁵⁻¹⁷ and present in samples of human blood.^{18, 19} Concerns about the potential environmental and toxicological impact of PFASs led to a phase out on the production of PFASs in AFFFs.²⁰ Additionally, the US EPA established a health advisory of 70 nanograms per liter for PFOA and PFOS.²¹ Nonetheless, PFAS concentrations with 3-4 orders of magnitude higher than the health advisory have been detected in groundwater and surface waters surrounding military fire training areas²² AFFFs containing PFAS continue to be used^{23, 24} but there is a search for fluorine-free AFFFs.^{25, 26}

Although little is known about the hydrocarbon surfactants in AFFFs, peer-reviewed literature⁷ lists alkyl amidobetaines, alkyl glucosides, alkyl sulfates, alkyl coco amidoglycinates, alkyl amino dipropionates and ethoxylated octylphenol as classes of hydrocarbon surfactants in AFFFs.⁷ Other literature^{27, 28} lists an additional four common classes of hydrocarbon surfactants in AFFFs, including alkyl ether sulfates, sulfobetaines, olefin sulfonates, and linear alkyl benzene sulfonates. However, no experimental data on hydrocarbon surfactants in AFFFs or AFFF-impacted groundwater exists. Hydrocarbon surfactants are surface active agents that can help reduce surface tension,²⁷ enhance²⁹ and stabilize foaming, or help as freeze protection agents in AFFFs.^{27, 28, 30} Hydrocarbon surfactants are classified as anionic, cationic, non-ionic or amphoteric.³¹ Anionic surfactants are negatively charged in aqueous solutions and usually contain sulfates, sulfonates, carboxylates or phosphates.^{31, 32} The most produced anionic surfactants by volume include fatty acid

soaps, linear alkyl benzene sulfonates, alkyl ether sulfates and alkyl sulfates.³²

Cationic surfactants are positively charged in aqueous solutions and usually contain ammonium compounds.³² Amphoteric surfactants contain both negative and positive charges and include two main groups, betaines and fatty alkyl imidazolines.³² Non-ionic surfactants have no charge and do not ionize in aqueous solutions.^{31, 32}

Occurrence of hydrocarbon surfactants is reported for various aquatic environments including oil,³³ fracking operations,³⁴ ocean water due to the use of oil dispersants,³⁵ municipal wastewater³⁶, and sewage sludge,^{37, 38} but not in fire-fighter training areas impacted by aqueous film forming foams (AFFFs). To date there are no data on hydrocarbon surfactants in AFFFs or for AFFF-contaminated groundwater, therefore their presence and possible persistence in AFFF-contaminated groundwater was never investigated.

The analysis of surfactants in environmental water samples, typically involves some type of sample extraction followed by liquid chromatography tandem mass spectrometry (LC-MS/MS).^{34, 39-42} LC-MS/MS is well suited for the study of surfactants with known masses and retention times (targets) based on the commercial availability of their analytical standards. However, for a less biased and more complete screening of surfactants, high resolution mass spectrometry (HRMS) offers the additional advantages of detecting accurate masses of suspect surfactant classes and for yet unknown (non-target) surfactant classes.⁴³ For example, high resolution mass spectrometry has already been used for the identification of surfactants in fracking fluids.^{34, 44, 45}

A beneficial characteristic of surfactants is that they occur as homologous series of mass and retention-times. One known method for identifying such series of ions with pre-defined mass differences is achieved by Kendrick mass defect (KMD) plots.⁴⁶⁻⁴⁹ However, another unsupervised computational method to detect such homologous series patterns without pre-defined mass differences has recently been proposed.⁵⁰

At present, there is considerable attention focused on the treatment of AFFF-contaminated groundwater and surface water, but that focus is only directed on the removal of PFASs.^{51, 52} Excess amounts of foaming can be seen in many lakes and groundwater at or near military sites where AFFFs were used.⁵³ There is no information on what fraction of the foaming is caused by hydrocarbon surfactants. More information on the occurrence and nature of hydrocarbon surfactants in AFFF contaminated water is needed since hydrocarbon surfactants likely compete with PFASs for removal onto granulated activated carbon^{40, 54} or ion exchange resins⁵⁵ and for oxidants during in-situ chemical oxidation depending on their chemical characteristics.⁵⁶ The high oxygen demand can drive systems anaerobic and kill the organisms used to treat sewage,⁵⁷ which can affect waste water treatment plants and end up in drinking water.

Many of the hydrocarbon surfactants listed in AFFF literature^{7, 27} are aerobically biodegradable^{31, 58} but some, may persist under anaerobic conditions.⁵⁸ Toxicity to aquatic organisms vary depending on the type of surfactants (cationic, anionic, non-ionic) and whether the alkyl chain is linear or branched.³² In general, aquatic toxicity for increases with alkyl and ethoxylate chain length.³²

According to CESIO (2000), the surfactants mentioned in AFFF literature, are classified as Irritant or Harmful.³² With the increasing demand of fluorine-free foams, the probability of using hydrocarbon based surfactants is high.⁵⁹⁻⁶¹ Data on the occurrence and persistence of hydrocarbon surfactants in AFFF-contaminated groundwater may may also be used to enhance the selection of surfactants for future inclusion into fluorine-free fire-fighting foams.^{59, 60}

The objective of this study was to use the semi-automated homologous series detection tool method for elucidating suspect surfactants in eight AFFFs and 10 AFFF-contaminated groundwaters collected from fire-fighter training areas source zones on nine US military bases. The AFFFs included, four 3M AFFFs and four fluorotelomer-based AFFFs including, Buckeye, Ansul, ChemGuard, and National Foam. All samples were analyzed by liquid chromatography quadrupole Time of flight mass spectrometry (qTOF-MS). Suspect screening on AFFFs and AFFF-impacted groundwater was performed using a screening list of hydrocarbon surfactants from the Norman suspect list exchange database and the enviMass workflow for data processing. The suspect list includes some degradation products, none of which were identified. Any non-target analysis for unknown surfactant series, degradation products, and quantification of identified series was beyond the scope of this study.

2. Experimental Section

2.1 Samples

Seven reference materials (Table 1) were donated by an AFFF manufacturer and capture some of the classes listed in AFFFs, including, alkyl amine oxides, alkyl poly glucosides, cocamidopropyl hydroxysultaines, alkyl sulfates and alkyl ether sulfates.^{7, 27} The material safety data sheets (MSDS sheets) revealed the chemical structure and/ or CAS number. The seven reference materials were diluted 100,000-fold in methanol. Blanks consisted of 30% methanol (v/v) in water and were run between the reference hydrocarbon surfactant samples to ensure no instrumental contamination was present and for the purpose of background subtraction.

The reference material analyses were performed on a Shimadzu LC-30AD (Columbia, MO) liquid chromatograph fitted with a Zorbax propylamine (NH₂) and Zorbax silica guard column in line with a C18 analytical column.⁸ The propylamine guard column is needed for isolating the nonionic surfactants (see Supporting Information). The liquid chromatograph was interfaced with a qTOF AB Sciex (Framingham, MA) TripleTOF 5600+ with electrospray ionization (ESI) operated in positive and negative modes. MS/MS data were collected in the data dependent-acquisition mode. The HRMS resolution was 35,000 with a cycle time of 1500 ms and an accumulation time per spectrum of 250 ms. Ions selected for fragmentation were prioritized by peak intensity. Data on the AFFF and AFFF-contaminated groundwater were collected for a previous study using the same chromatographic and HRMS conditions listed above.⁸ In brief, the AFFFs consisted of four 3M AFFF

formulations manufactured in 1988, 1989 and two formulations manufactured in 1993 along with four fluorotelomer AFFF formulations manufactured in 2003, 2009, 2010 and 2012. The AFFFs were obtained from an archive of AFFF samples from U.S. military bases near fire training source zones located near aircraft runways, as described by Place and Field 2012.¹² Groundwater samples analyzed in this study were collected by third parties as described by Backe et al. 2013.¹¹ Eight out of ten groundwaters (all except Sites G and J) were obtained approximately 20 years since the last releases of AFFF at these sites. In contrast, groundwater from sites G and J were obtained in 1999 and stored frozen until the time of this study. The source zones near fire-fighter training areas are located in close proximity to the bases' aircraft runways.

2.2 Workflow

Preliminary attempts to use Kendrick Mass Defect plots to screen for homologous series in AFFF and AFFF-contaminated were unsuccessful because the plots were too complex (Figure 1). For this reason, an alternate workflow incorporating enviMass was used.

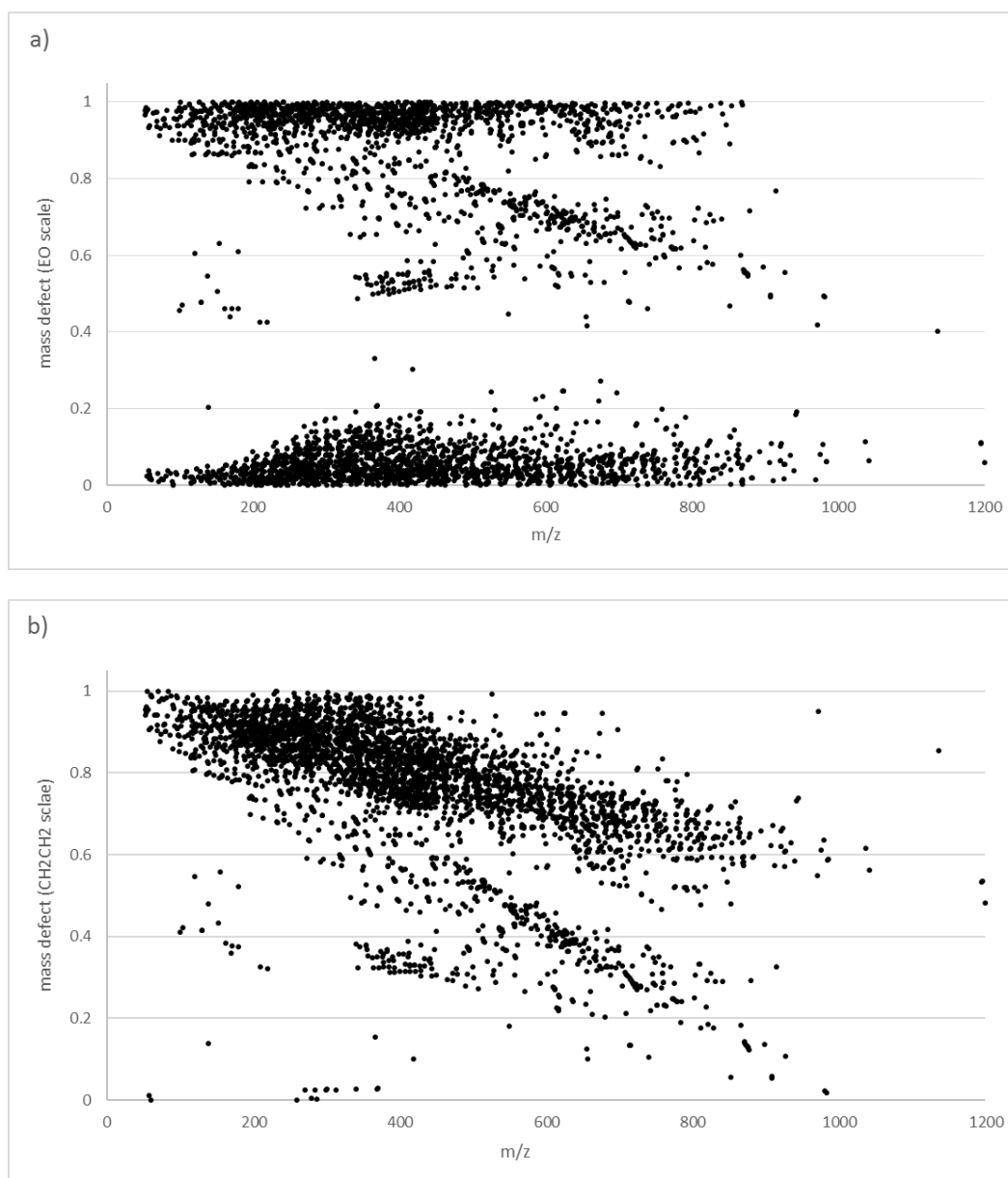


Figure 1. Preliminary attempts to search for homologous series in Kendrick Mass Defect Plots

All files acquired in positive and negative mode were converted from proprietary format (.wiff files, SCIEX) to open format (.mzXML) with ProteoWizard (version 3.0) and uploaded to EnviMass.

A two-stepped procedure was implemented (Figure 2), which involved establishing confidence in enviMass using Reference Materials followed by suspect screening of AFFF and groundwater files.

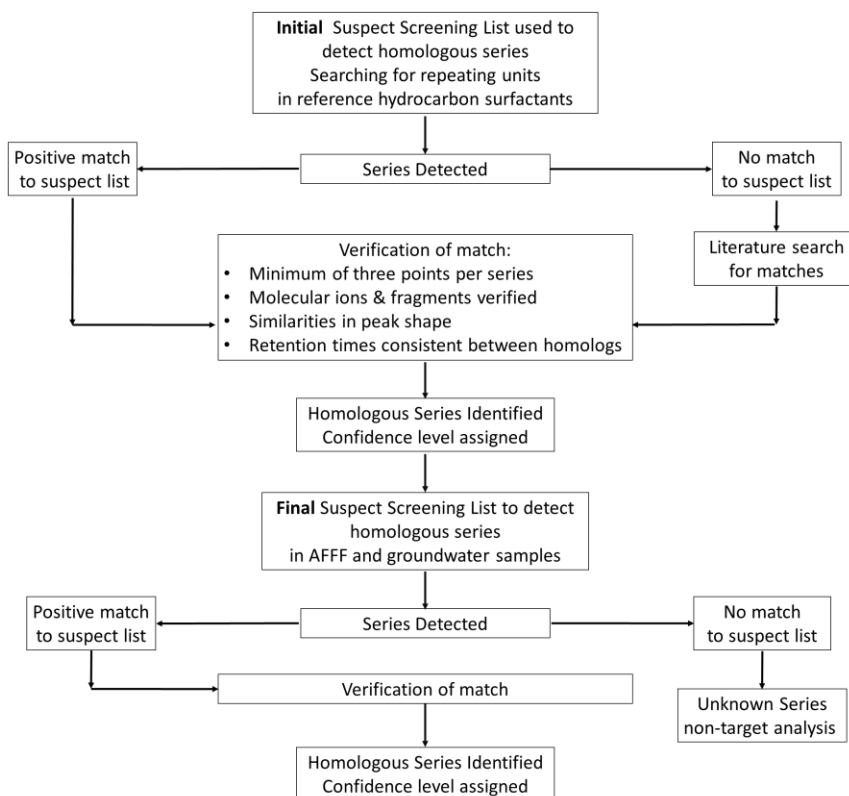


Figure 2. Workflow indicating steps to create final suspect list from database and Reference Materials, use of suspect list to detect homologous series of surfactants in AFFF and AFFF-contaminated groundwater.

A suspect list of 811 hydrocarbon surfactants was compiled from the NORMAN database,⁶² and literature,⁶³⁻⁶⁵ which included data on molecular ions, formula, fragment ions, and adducts. The initial suspect list included all surfactants listed in Pabon and Corpart⁷ and from Thomas,²⁷ except for sulfobetaine, sodium alpha olefin sulfonates, which were manually derived by assuming an alkyl group range of C₈₋₁₆. In addition, octylphenol polyethoxylate carboxylates were added manually to the database assuming ethoxylate units ranging from EO₁₋₂₀.⁶⁵

Surfactants were chosen based on the common characteristic repeating units limited to alkyl [CH_2CH_2 ; $\Delta m/z$ 28], ethoxylate [$\text{CH}_2\text{CH}_2\text{O}$; $\Delta m/z$ 44], and glucoside [$\text{C}_6\text{H}_{12}\text{O}_5$; $\Delta m/z$ 162] repeating units. The repeating unit of CH_2CH_2 instead of CH_2 was selected after initial plots were too complex, especially for groundwater. Note that a class may have more than one repeating group. The suspect list did not include PFASs nor siloxane-based surfactants.

The enviMass homologous series detection tool was then queried to search for masses that differed by alkyl, ethoxylate, and glucoside repeating units. A *positive match* indicated that a homologous series in the sample matched a series in the suspect screening list. When a homologous series had at least three homologs, the series was further verified using Masterview 2.2 (SCIEX) for peak shape and fragmentation verification to those for series in a database or literature. Peak shapes and differences in retention times between the homologs were required to be consistent. Once all criteria were verified, the series was successfully assigned a confidence level (Table 4).⁶⁶ In summary, a level 1 confidence represents a confirmed structure with a reference standard with MS, MS/MS and retention times matching. In the case of this study using suspect screening with no reference standards, the confidence levels fall in level 2 and 3 (Table 4) in which the MS, MS/MS has been matched to a database.⁶⁷

In the case where a homologous series in the Reference Materials gave *no match*, a literature MetFrag database⁶⁸ search was performed to find a match to the masses detected. The match then had to undergo the same verification process as described above. Once the homologous series was identified, a confidence level was

assigned, and the series was added to the final suspect screening list. After verification of the homologous series in the Reference Materials and optimization of the initial suspect screening list and enviMass parameters, the final suspect surfactant list was ready for the analysis of AFFF and groundwater files.

The AFFF and groundwater open format files (.mzXML) were treated in the same manner as reference materials, except that the detected homologous series that resulted in a *no match* with the suspect list were flagged for future non-target analysis. Non-target analysis of unknown series was beyond the scope of the present study.

3. Results and Discussion

3.1 Reference Materials

All seven reference materials underwent suspect screening to ensure that the use of enviMass detected each of the hydrocarbon surfactant classes stated in the MSDS sheets for each Reference Material. Once enviMass is queried to search for a repeating unit, enviMass plots all possible series that meet the criteria for a homologous series (e.g. at least three masses per series and that differ by the specified repeating unit, with a systematic change in retention time). Complexity is further reduced by the verification steps identified in the workflow (Figure 2). Final plots generated by enviMass contain only the identified suspect homologous series (Figure 3). Other series present in Reference Materials were not further investigated, as the

main objective when analyzing the reference materials was to identify the main series as described on their respective MSDS.

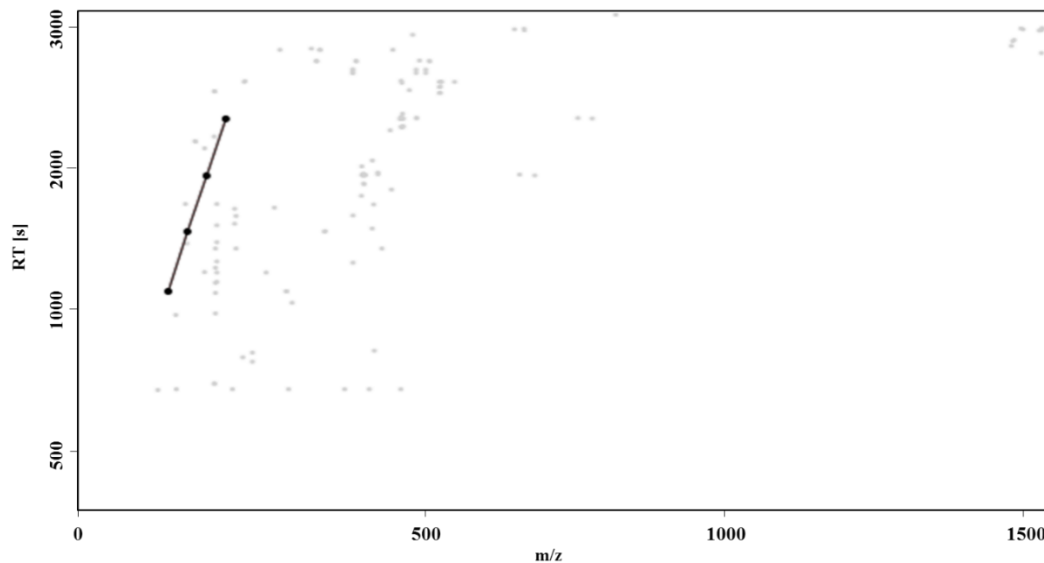


Figure 3. Homologous series of alkyl amine oxides in Reference Material 1 is represented by a nearly vertical line.

All the major hydrocarbon surfactant classes listed on the MSDS were detected (Table 1). The hydrocarbon surfactants identified with confidence level 2 in Reference Materials 1-7 are reported in AFFFs.^{7, 27, 30} EnviMass provides information on the number of homologous series as well as the number of homologs within each series (Table S1), which goes well beyond the information provided by the MSDS. For example, Reference Material 1 is listed as lauramine oxide on the MSDS and hence lead to a homologous series of alkyl amine oxides with even numbers of alkyl carbons (e.g. C_{10,12,14,16}; Table 1). Reference Material 2, labeled as an alkyl polyglucoside solution (Table 1), contained three series. The first series had a range of carbons in the alkyl unit (C₉₋₁₁) with only one glucose unit (Figure 4a) while the other series had an alkyl chain of C₁₁ with three glucose units (Figure 4b). It is

important to note that the series found on Reference Material 2 were found by searching for both alkyl and glucose repeating units, which would not be possible when using standard Kendrick plots. Reference Materials 3-6 contained only a single series characterized by an alkyl repeating unit (Table 1). EnviMass indicated that in Reference Material 3, (cocamidopropyl hydroxysultaine) only existed as odd carbon chain length series, whereas alkyl sulfates in Reference Material 4 had only even numbers of carbons (Table 1). Reference Materials 5 and 6 were also alkyl sulfates but with even and odd numbers of carbons in the alkyl chain (Table 1). Although the search relied on CH_2CH_2 , even and odd numbers of carbon homologs were detected for a series. EnviMass detects multiple alkyl series differing by CH_2CH_2 , but manual reduction combines them into one unique series, which is why even and odd homologs are reported. Reference Material 7 contained one alkyl ether sulfate homologous series with repeating EO units (Figure 5).

Table 1. Hydrocarbon surfactant classes detected in seven Reference Materials and their respective alkyl (C_n), ethoxylate (EO_n), and glucose (GLUC_n) repeating units. Multiple repeating units are separated by “/”.

Class [repeating unit]	General Structure	Reference Material 1 (Stepan Ammonix Lo)	Reference Material 2 (BASF APG 325 N)	Reference Material 3 (Cola Teric CSB)	Reference Material 4 (Colonial TEALS)	Reference Material 5 (Lubrizol Sulfochem NADS-40)	Reference Material 6 (Colonial SOS)	Reference Material 7 (CalFoam ES-302)
Alkyl amine oxide [C _n]		10,12,14,16	ND	ND	ND	ND	ND	ND
Glucoside [C _n / GLUC _n]		ND	9,10,11/1 10/1,2,3 11/2,3,4	ND	ND	ND	ND	ND
Cocamidopropyl hydroxysultaine [C _n]		ND	ND	7,9,11,13,15	ND	ND	ND	ND
Alkyl sulfate [C _n]		ND	ND	ND	12,14,16	8-12	8-11	ND
Alkyl ether sulfate [C _n /EO _n]		ND	ND	ND	ND	ND	ND	12/1-11

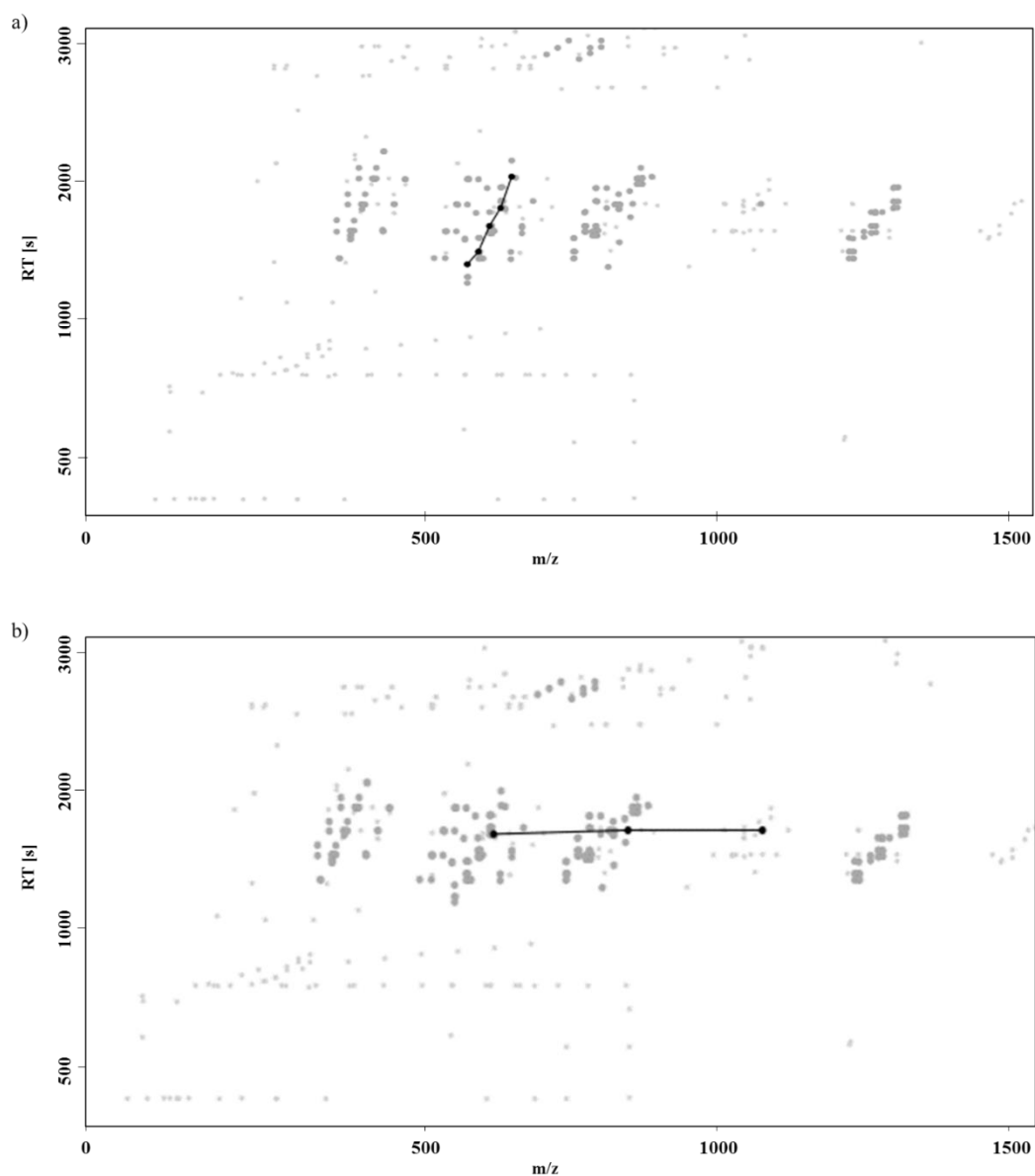


Figure 4. Homologous series of a) repeating alkyl units represented by a nearly vertical line in and b) repeating glucoside units represented by a horizontal line in Reference Material 2, an alkyl polyglucoside. Other homologous series are present in the Reference Material, but were not identified since the main series indicated on the MSDS (dark symbols and line) was successfully identified.

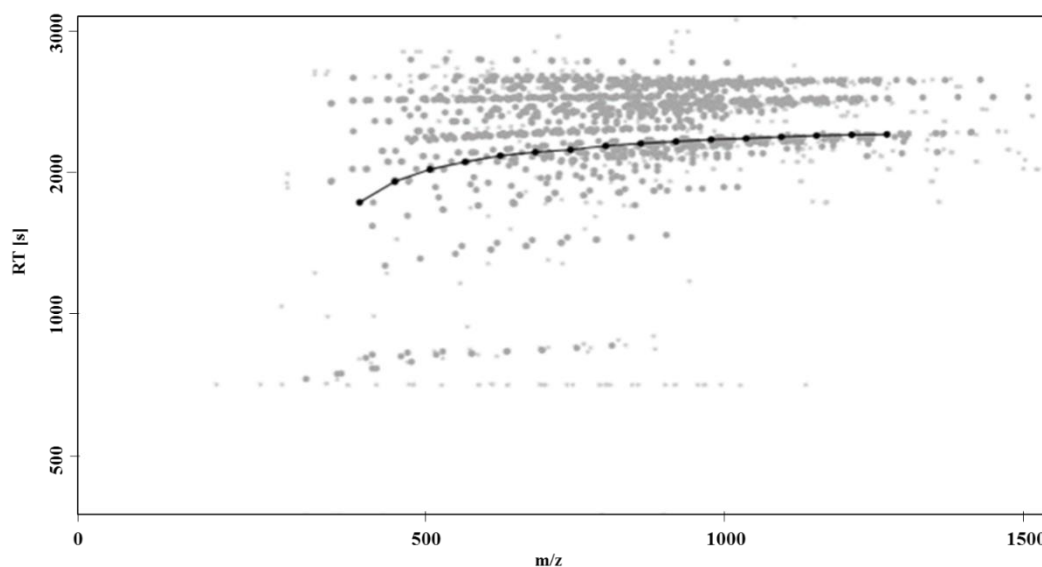


Figure 5. Homologous series in Reference Material 7 (CalFoam ES302) characterized by repeating EO units and a curve. The main homologous series indicated on the MSDS is highlighted in black.

Due to the complexity of mixtures such as those in AFFFs, series plotted in enviMass gave characteristic retention time patterns for the various types of repeating units that was a useful diagnostics tool for classifying homologous series of hydrocarbon surfactants. For example, homologous series characterized by repeating alkyl units produced nearly vertical lines (Figure 3 and Figure 4a), repeating glucose units produced horizontal lines (Figure 4b), and repeating EO units gave curves (Figure 5). The characteristic curves are attributed to the chromatographic separation of repeating units. For example, alkyl homologs elute approximately every two min. while ethoxylate and glucoside repeating units elute approximately every 10 to 30 s.

3.2 Hydrocarbon surfactants in AFFFs

A total of nine hydrocarbon surfactant classes were identified with confidence level 2-3 in the eight AFFFs and of those, seven were common to both 3M and telomer AFFFs (Table 1).

The homologous series of octylphenol polyethoxylates found in AFFFs (EO₃₋₂₀) is consistent with AFFF patents (octylphenol polyethoxylate with EO ≥ 10).²⁸ Similar ranges in EO units between stored AFFFs and patent literature indicates stability of the octylphenol polyethoxylates over the long period of AFFF storage, which ranged up to 20 years since the time of AFFF manufacture (1988-2012; Table 1).

Nonylphenol polyethoxylates and its degradation products, mono- and diethoxycarboxylates were on the suspect list but were not detected in any AFFFs. An example of homologous series plots with repeating EO units and the final series after data reduction in Buckeye AFFF is seen in Figure 6.

Linear alcohol ethoxylates (EO₂₋₁₀) appear in 3M AFFFs and Buckeye (Table 1). Linear alcohol ethoxylates are added to AFFFs to reduce surface tension.²⁷ Ethoxylated cocoamines (C₁₄₋₁₇EO₃) were only detected in telomer-based AFFFs (Buckeye and National foam).

Homologous series of alkyl ether sulfates, which are characterized as “foam boosters,”²⁸ were found in seven out of eight AFFFs due to detection of their repeating alkyl (C₁₅₋₁₇EO₁) and EO units (C₁₄EO₁₋₃ and C₁₂EO₁₋₈) by enviMass. Had the search relied on only one repeating unit (e.g., C_n), alkyl ether sulfate homologs with EO units (i.e. C₁₄EO₁₋₃) would have gone undetected. Patent literature for AFFFs reports alkyl ether sulfates with C₆₋₁₀ alkyl groups and two ethoxylate units

EO₂,²⁸ yet homologous series with more than two EO units (EO₁₋₈) were also detected (Table 2). Alkyl amido dipropionates (C_{12,13,14}) were found in only Buckeye and Chemguard, which are telomer-based AFFFs (Table 2).

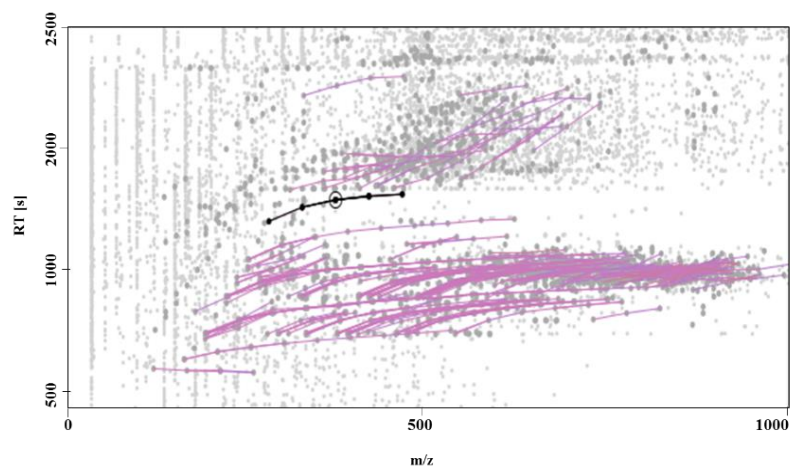
Linear alkyl benzene sulfonates (C₁₀₋₁₃) were detected in six out of eight 3M and telomer-based AFFFs (Table 2). Alkyl sulfonates (C₈₋₁₂) and alkyl sulfates (C₈₋₁₂) were detected in three and six out of eight 3M and telomer-based AFFFs (Table 2). Alkyl sulfonates²⁸ (C₆₋₁₀) and linear alkyl benzene sulfonates²⁹ (C₁₀₋₁₄) are listed in AFFF patent literature. All three classes of sulfonate surfactants are known as foaming agents.⁶⁹

Polyethylene glycols were detected by their repeating EO units. Polyethylene glycols were found in five out of eight AFFF with similar EO ranges (EO₈₋₁₃; Table 1).

The suspect surfactants detected in the archived AFFFs are listed in AFFF patents,²⁸ and peer-reviewed literature.^{7, 27} Hydrocarbon surfactants are effective at reducing interfacial tension⁷⁰, increase viscosity,³⁰ help solubilize other AFFF components^{28, 71} and are effective foamers.⁶⁹ An additional surfactant class, alkyl amido betaines listed in AFFF literature as corrosion inhibition additives and foam boosters⁷² was detected but did not meet the minimum requirements to be reported as a positive detection. The alkyl polyglucosides in the suspect list obtained from AFFF literature^{7, 27} were not detected in the archived AFFFs. However, other unidentified glucosides in AFFFs (data not shown) were detected, which indicates that other glucoside-based surfactants were used. Additional unknown series characterized by repeating alkyl, and ethoxylate units remain unidentified in the AFFFs, but

identifying surfactants not in the suspect list (non-target analysis) was beyond the scope of the study. Manual data reduction is required to eliminate redundant series so that an accurate assessment of the number of remaining unidentified, unique series can be made. Thus, the exact number of unknown series is difficult to estimate. Additional filters for retaining only monoisotopic, most intense isobaric and most intense co-eluting series of different adducts of the same homologous nontarget compound have been added to enviMass in the meantime, but were not available at the time of this research.

a)



b)

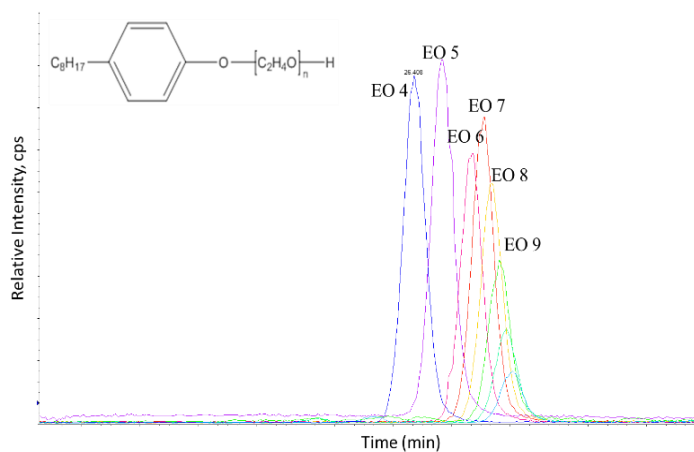


Figure 6. Homologous series repeating by ethoxylate units $[\text{CH}_2\text{CH}_2\text{O}]$ in Buckeye 2009 a) before data reduction plotted by enviMass (lightgrey: all picked peaks, darkgrey: peaks combined into any series, pink lines: peak series with ethoxylate mass units and b) series peak shapes of ethoxylate homologous series after data reduction verified with Masterview 2.2 (SCIEX)

Table 2. Hydrocarbon surfactant classes classified by repeating units in 3M and fluorotelomer-based AFFFs (Buckeye, Ansul, Chemguard, National Foam). Multiple repeating units are separated by “/”. *ND= Non Detected, which means that no homologous series matched that of the suspect list. Reports of surfactants present in AFFF reported by a) Pabon et al. 2002 b) Thomas Marin 2012 c) U.S. Patent No. 6,015,838*

Class	3M 1993a	3M 1993b	3M 1988	3M 1989	Buckeye 2009	Ansul 2012	Chemguard 2010	National Foam 2003
Octylphenol polyethoxylate ^{a,b} EOn	ND	ND	3-16	ND	4-9	4-10	4-20	ND
linear alcohol ethoxylate ^c Cn / EOn	10/2-10	10/2-10	ND	ND	10/2 -7	ND	ND	ND
Ethoxylated Cocoamine ^c Cn / EOn	ND	ND	ND	ND	14,15,16/3	ND	ND	14,15,16,17/3
Alkyl ether sulfate ^b Cn / EOn	15,16,17/ 1 12/1-8	15,16,17/1 12/1-7	ND	15,16,17/1 12/1-6	14/1,2,3 12/1-7	15,16,17/1	14/1,2,3 12/1-10	15,16,17/1
Alkyl amido- dipropionates ^b Cn	ND	ND	ND	ND	12,13,14	ND	12,13,14	ND
linear alkyl benzene sulfonate ^b Cn	11,12,13	10,11,12,13	ND	10,11,12,13	10,11,13	10,11,12,13	ND	10,11,12,13
Alkyl sulfonates ^b Cn	8,9,10	ND	ND	9,10,12	ND	ND	ND	9,10,12
Alkyl sulfates ^{a,b,c} Cn	8,10,12	8,10,12	ND	8,10,12	8,9,10,11,12	ND	8,9,10,12	8,9,10,11,12
Polyethylene Glycol EOn	8-13	ND	8-13	8-13	8-13	10-13	ND	ND

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3.3 Hydrocarbon Surfactants in Groundwater

Octylphenol polyethoxylates were the most frequently detected hydrocarbon surfactant in AFFF-impacted groundwater sites (eight out of 10 samples; Table 3). To our knowledge, this is the first report of octylphenol polyethoxylates in AFFF-impacted groundwaters and to link their presence to AFFF. The homologs detected

were comprised of EO₃₋₁₁ (Table 3), which is a narrower range than those in AFFFs (EO₃₋₂₀; Table 1). Biodegradation of alkylphenol polyethoxylates may have resulted in shorter EO chains,^{36, 73-75} which indicates that some biodegradation of octylphenol polyethoxylates may have occurred after AFFF application (≥ 20 years). Degradation products including octylphenol mono-, di- and triethoxycarboxylates and octylphenol were not detected. Octylphenol polyethoxylates were not among the reference materials, but are listed as components of AFFFs.^{7, 27} Octylphenol polyethoxylates persist in other environments including sediments;⁷⁶ surface waters including the Great Lakes,⁷⁷ river waters,⁷⁸ and estuaries;⁷⁶ as well as in municipal wastewaters^{79, 80 81}

Linear alcohol ethoxylates were detected in four of ten groundwaters (Sites G, H, I, J; Table 3). The linear alcohol ethoxylates are characterized as having a C₁₀ alkyl chain and two to eight EO units, which is similar to those detected in AFFFs (Table 1). Little difference in the homolog distributions between groundwater (Table 2) and AFFFs (Table 1) indicates minimal biodegradation even after ≥ 20 years despite reports of aerobic^{41, 82, 83} and anaerobic⁸² biodegradation. Alcohol ethoxylates have previously been reported in sewage sludge,^{64, 84} wastewaters and drinking water.⁸⁵

Ethoxylated cocoamines, previously reported in sewage sludge⁸⁴ and for enhanced oil recovery,³³ were detected only in one groundwater (C₁₄₋₁₆, Site, J; Table 3) and in two fluorotelomer-based AFFFs (Table 2). The chain lengths observed in groundwater (C₁₄₋₁₆) are identical to those in National Foam AFFF (Table 2). Ethoxylated cocoamines have a pK_a⁸⁶ of ~ 15 , which indicates that the cationic form dominates at pHs < 9 , which is typical of aquifers. For this reason, ethoxylated

cocoamines, will likely associate with soil and/or sediment by cation exchange, which potentially explains why they are observed in only one source-zone groundwater (Site J; Table 3).

Alkyl ether sulfates were detected in two of ten groundwaters (Sites I and J) and, unlike the homologous series detected in AFFFs with alkyl and ethoxylate repeating units (Table 2), the homologous series in groundwater are characterized by a single alkyl chain length (C₁₅ or C₁₆) with repeating EO units (EO₁₋₆ for Site I and EO₈₋₁₂ for Site J; Table 3). Similar ethoxylate chain lengths in groundwater (Table 3) and AFFFs (Table 2) is attributed to a lack of biodegradation even though alkyl ether sulfates degrade aerobically^{83, 87-89} to homologous series of polyethoxylated glycol sulfates and are mineralized under anaerobic conditions.^{58, 90} Transformation products of alkyl ether sulfates, polyethoxylated glycol sulfates, were not in suspect lists but could contribute to unknown homologous series of ethoxylates that were detected in all groundwaters (data not shown). Alkyl ether sulfates are previously reported in river waters,^{87, 91} wastewaters,⁹¹ and sediments.⁹²

Two hydrocarbon surfactants were found in groundwater but not AFFFs nor the reference materials included diethanolamides and alkyl amido betaines (Table 3). Diethanolamides, which are reported biodegradable in both aerobic and anaerobic conditions,^{41, 84, 93} were found in seven of ten groundwaters with alkyl chains ranging from C₇₋₁₅ (Table 3). Alkyl amido betaines are also biodegradable under both aerobic and anaerobic conditions,⁹³ but were detected with alkyl chains C₄₋₇ in three groundwaters (Sites F, H, and J ; Table 3). Diethanolamides are also reported for use

in enhanced oil recovery applications,³³ while alkyl amido betaines are reported for use in personal care products.⁹⁴

Alkyl amido dipropionates were detected in two groundwaters (Site F and J; Table 3) even though they are aerobically biodegradable.⁹⁵ There is limited data on anaerobic biodegradation; however, one report indicated only minimal degradation⁹⁵ (2.5% of theoretical production during 56 days). The chain lengths detected in groundwater (Table 3) are shorter than those detected in AFFFs (Table 2). Nonetheless, alkyl amido dipropionates remain persistent in current groundwater conditions.

Linear alkyl benzene sulfonates are detected in only two groundwaters even though they were found in eight of 10 AFFFs (Table 2). Although linear alkyl benzene sulfonates biodegrade under both aerobic and anaerobic conditions,⁹⁶ they are still found in municipal wastewater and sludge⁸⁴ and are persistent in groundwater impacted by wastewater.⁹⁷⁻⁹⁹ In contrast, alkyl sulfonates, alkylsulfates, and polyethylene glycols were not detected in any of the source-zone groundwaters, which indicates that they may have been used in the AFFF deployed at these sites or that they biodegraded. Alkyl sulfates and alkyl sulfonates are readily mineralized under aerobic and anaerobic conditions.^{89, 93, 100, 101} while polyethylene glycols are readily biodegraded under aerobic conditions.⁸³

Additional unknown homologous series containing the mass differences possibly corresponding to alkyl, glucoside, and ethoxylate repeating units were present in source zone groundwaters but would require efforts for unambiguous identification.

The eight surfactants classes found in AFFF-contaminated groundwater indicate their persistence under prevailing groundwater conditions at the ten AFFF source zones. Furthermore, the hydrocarbon surfactants detected in this study may have entered the groundwater through other sources. For example, hydrocarbon surfactants could enter the groundwater from comingled waste that were used for training fires. Although hydrocarbon surfactants occur in wastewater, waste water treatment plant effluents are not likely to impact the fire-training area source zones sampled for this study. Aircraft deicers and anti-icing fluids, which contain linear alcohol ethoxylates,¹⁰² and polyethylene glycol,^{103, 104} are a potential source at military sites but only at northern latitudes. Sites C, E, F, G, and H (Table 3) are in locations where the use of deicers is possible and, thus, deicers cannot be ruled out a source of some of the hydrocarbon surfactants. Although not all military sites are located in locations with cold weather conditions, planes may need treatment prior to flying to cold-weather locations.

The persistence of hydrocarbon surfactants at fire training sites may be due to anaerobic conditions that result from the organic carbon loading (e.g., surfactants, solvents, fuels) associated with repeated applications of AFFF,²⁴ which have high biological oxygen demand (e.g., ~650,000 mg/L).^{57, 105} Is ref 85 about BOD? While there are anaerobic biodegradation pathways for many hydrocarbon surfactants, most studies utilize activated sludge (aerobic) or anaerobic sludge as the source of the microbial consortium, which may not reflect the microbial communities in AFFF-contaminated aquifers. Evidence of biodegradation, as indicated by a shift to shorter-

chain homologs, requires further investigation and the use of non-target HRMS to identify hydrocarbon surfactant degradation products.

Table 3. Hydrocarbon surfactant classes identified by repeating units in groundwater. Multiple repeating units are separated by “/”. *ND= Non Detected, which means that no homologous series matched that of the suspect list.* Surfactants in AFFF literature listed by a) Pabon et al. 2002 b) Thomas Marin 2012 c) U.S. Patent No. 6,015,838

Class	A	B	C	D	E	F	G	H	I	J
Octylphenol polyethoxylate ^{a,b,c} EOn	4-11	4-11	4-9	ND	4-11	ND	7-11	5-10	5-9	3-11
linear alcohol ethoxylate ^c Cn / EOn	ND	ND	ND	ND	ND	ND	10/2-8	10/2-7	10/3-7	10/3-8
Ethoxylated cocoamine ^c Cn	ND	ND	ND	ND	ND	ND	ND	ND	ND	14-16
Alkyl ether sulfate ^b Cn / EOn	ND	ND	ND	ND	ND	ND	ND	ND	15/1-6	16/8-12
Diethanolamide Cn	ND	7, 9, 11, 13	7, 9, 11, 13	7, 9, 11, 13	11, 13,15	7, 9, 11, 13	ND	7,11, 13, 15	9,11,13	ND
Alkyl amido betaine ^b Cn	ND	ND	ND	ND	ND	4,5,6,7	ND	4,5,6	ND	4,5,6
Alkyl amido dipropionate ^b Cn	ND	ND	ND	ND	ND	8,10,12	ND	ND	ND	6,8,10
Linear alkyl benzene sulfonate ^b Cn	ND	ND	ND	11,12, 13,14	ND	ND	ND	ND	10,11,13, 14	ND

Table 4. Master Table listing all hydrocarbon surfactant classes found in AFFF and Groundwater and their respective error (ppm) and confidence level.

Class	n	Precursor mass with adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Octylphenol polyethoxylate EOn	3	356.28	356.2797	0.6	3	2a
	4	400.306	400.3054	-0.8	2a	2a
	5	444.332	444.332	0.1	2b	2a
	6	488.358	488.3556	-5.3	2a	2a
	7	532.384	532.3837	-1.4	2a	2a
	8	576.411	576.4096	-1.7	2a	2a
	9	620.437	620.4357	-1.8	2a	2a
	10	664.463	664.4617	-2.0	2a	2a
	11	708.489	708.4876	-2.4	2a	2a
	12	752.515	752.5135	-2.6	3	NA
	13	796.542	796.5399	-2.2	3	NA
	14	840.568	840.5669	-1.2	3	NA
	15	884.594	884.5926	-1.7	3	NA
	16	928.62	928.6182	-2.3	3	NA
	17	972.647	972.6454	-1.2	3	NA
	18	1016.673	1016.672	-1.2	3	NA
	19	1060.699	1060.699	-0.4	3	NA
	20	1104.725	1104.725	-0.6	3	NA
linear alcohol ethoxylate Cn / EOn	C10 E2	264.253	264.2351	-1.0	2a	3
	C10 E3	308.280	308.2794	-0.4	2a	3
	C10 E4	352.306	352.3052	-1.5	2a	3
	C10 E5	396.332	396.3313	-1.6	2a	3
	C10 E6	440.358	440.3567	-3.4	2a	3
	C10 E7	484.384	484.3829	-3.1	2a	3
	C10 E8	528.411	528.4086	-3.9	2a	3
	C10 E9	572.437	572.4352	-2.8	2a	NA
	C10 E10	616.463	616.4607	-3.7	2a	NA
Ethoxylated cocoamine Cn/ EOn	14	324.23834	324.2381	-0.8	2a	2a
	15	338.25399	338.2529	-3.1	2a	2a
	16	352.26964	352.269	-2	2a	2a
	17	366.28598	366.2854	-1.6	2a	NA

Class	n	Precursor mass with adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Alkyl ether sulfate Cn / EOn	C12 EO8	617.358	617.3582	0.9	2a	NA
	C12 EO9	661.384	661.3856	2.6	2a	NA
	C12 EO10	705.410	705.4084	-2.3	2a	NA
	C14 EO1	337.205	337.2053	-0.3	2a	NA
	C14 EO2	381.232	381.2319	0.8	2a	NA
	C14 EO3	425.258	425.2576	-0.6	2a	NA
	C15 EO1	351.221	351.2185	-7.3	2a	2a
	C15 EO2	395.247	395.2446	-6.8	NA	2a
	C15 EO3	439.273	439.2732	-0.6	NA	2a
	C15 EO4	483.300	483.2998	0.2	NA	2a
	C15 EO5	527.326	527.3257	-0.4	NA	2a
	C15 EO6	571.352	571.3522	0.0	NA	2a
	C16 EO1	365.237	365.2371	1.0	2a	NA
	C16 EO8	673.420	673.4206	0.5	NA	2a
	C16 EO9	717.446	717.4477	1.8	NA	2a
	C16 EO10	761.473	761.4727	0.0	NA	2a
	C17EO1	379.252	379.2524	0.0	2a	NA
Alkyl amido dipropionate Cn	4	218.139	218.1385	-1.0	2a	2a
	6	246.1699	246.1699	-0.3	2a	2a
	8	275.2090	275.2083	-2.9	2a	2a
	10	303.240	303.2405	0.4	2a	2a
	12	330.264	330.2642	1.0	2a	2a
	13	344.280	344.2793	-0.6	2a	NA
	14	358.295	358.2951	-0.2	2a	NA

Class	n	Precursor mass with adduct	observed m/z	Error (ppm)	Confidence Level AFFF	Confidence Level Groundwater
Linear alkyl benzene sulfonate C _n	10	297.153	297.1528	-0.5	2a	2a
	11	311.169	311.1687	0.2	2a	2a
	12	325.184	325.1846	0.9	2a	2a
	13	339.200	339.1999	0.0	2a	2a
	14	353.216	353.2177	6.0	NA	2a
Alkyl sulfonates C _n	8	199.137	199.1355	-9.2	2a	NA
	9	212.145	212.1442	-4.7	2a	NA
	10	222.122	222.1219	0.8	2a	NA
Alkyl sulfates C _n	8	209.085	209.0854	0.6	1	NA
	9	223.101	223.1009	-0.2	1	NA
	10	237.117	237.1166	-0.1	1	NA
	12	265.148	265.1479	-0.1	1	NA
Polyethylene Glycol EOn	8	388.254	388.2542	0.1	2a	NA
	9	432.280	432.2801	-0.5	2a	NA
	10	476.307	476.3063	-0.6	2a	NA
	11	520.333	520.3333	1.0	2a	NA
	12	564.359	564.3595	1.0	2a	NA
	13	608.385	608.3857	0.8	2a	NA
Alkyl amido betaine C _n	4	246.194	246.1938	-0.1	3	2a
	5	260.209	260.2077	-6.6	3	2a
	6	274.225	274.2273	7.9	3	2a
	7	288.241	288.2404	-1.2	2b	2a
Diethanolamine C _n	7	232.1907	232.1902	-2.1	NA	2a
	9	260.2215	260.222	1.9	NA	2a
	11	288.2533	288.2531	-0.7	NA	2a
	13	316.2846	316.2844	-0.8	NA	2a

NA= Not available indicating the homologous series was not present in either AFFF or Groundwater.

4. Conclusions

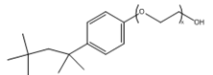
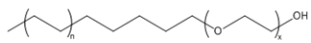
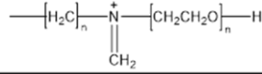
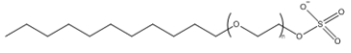
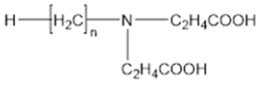
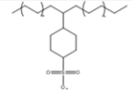
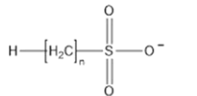
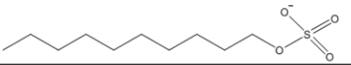
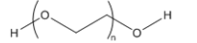
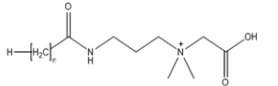
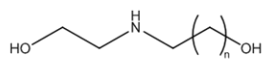
Given the similarities in the hydrocarbon surfactant compositions between 3M and telomer AFFFs, it may not be possible from a forensics point of view to distinguish which AFFFs were used at a given field site based on the hydrocarbon surfactant composition in groundwater. However, non-target identification may yield unique chemicals that could be used to identify AFFF sources.

AFFF-impacted groundwater discharges into surface waters where the hydrocarbon surfactants have the potential to contribute to foaming,⁵³ biodegrade aerobically to transformation products that might have the potential to adversely impact biota. In particular, short chain octylphenol mono- and diethoxylates and octylphenol are toxic to aquatic organisms with their ability to disrupt the endocrine system.

Hydrocarbon surfactants in AFFF-contaminated groundwater can compete with PFASs for ion exchange sites on resins,¹⁰⁶ on granulated activated carbon,⁵¹ and for oxidants during in-situ chemical oxidation.⁵⁶

One limitation of this study is that no concentrations of the hydrocarbon surfactants in groundwater were determined. However, the data indicate that hydrocarbon surfactants are persistent in groundwater, which indicates they might also exist in sediment, soil and biota at AFFF-contaminated sites. Future research is needed to document if hydrocarbon surfactants persist in AFFF-contaminated sediment, soil, and biota.

Table S5. Summary of surfactants detected in AFFFs and AFFF-impacted groundwater.

Surfactant	Structure	8 Archived AFFFs	Groundwaters
Octylphenol polyethoxylates		✓	✓
Linear alcohol ethoxylates		✓	✓
Ethoxylated cocoamines		✓	✓
Alkyl ether sulfates		✓	✓
Alkyl amido dipropionates		✓	✓
Linear alkyl benzene sulfonates		✓	✓
Alkyl sulfonates		✓	
Alkyl sulfates		✓	
Polyethylene glycols		✓	
Alkyl amido betaine			✓
Diethanolamines			✓

5. Acknowledgments

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