HALEY & ALDRICH PFAS TECHNICAL UPDATE

AFFF for firefighting

The latest research indicates that per- and polyfluoroalkyl substances (PFAS) may have potential adverse human health and environmental impacts. This has resulted in the creation of health-based standards, including mandatory state orders for various entities requiring investigation of potential PFAS contamination. The regulatory climate is evolving as the scientific and regulatory communities continue to learn about PFAS and their environmental and health impacts.

To make informed decisions about if, when, and how to investigate, potentially responsible parties must understand the use of PFAS in their existing and historical operations, including technical and operational details. Haley & Aldrich's PFAS Technical Updates will help you stay informed. States have been issuing PFAS assessment orders for entities such as water purveyors, airports, landfills, and specific manufacturing facilities. Some states are planning to continue to issue orders to various facilities (such as petrochemical and wastewater treatment plants in California) and to request additional sampling from impacted public water supply wells.

AQUEOUS FILM-FORMING FOAM (AFFF) FOR FIREFIGHTING

There are two main types of firefighting foam in use around the world. Firefighters use Class A foams to lower the surface tension of water, primarily for extinguishing structure fires and wildfires. They deploy Class B foams containing synthetic surfactants for





fires involving combustible liquids. One of the most common synthetic firefighting foams is aqueous film-forming foam (AFFF). AFFF was developed in the 1960s and is a water-based foam containing PFAS. It became the standard fire suppressant for the Department of Defense (DoD) in 1969 (Interstate Technology & Regulatory Council [ITRC] 2018). The active ingredients in AFFF include fluorinated alkyl surfactants and hydrocarbon surfactants. The fluorinated alkyl surfactants lower the surface tension, resulting in an aqueous film across the surface of liquid hydrocarbon fuel that extinguishes flames and forms a barrier that prevents reignition (Moody and Field, 2000). Firefighters use AFFF at their training centers, as well as where there are significant flammable liquids stored or used, including oil refineries, bulk fuel storage farms, fuel terminals, airports, and military facilities (ITRC, 2018).

PFAS IN AFFF

Manufacturers used two processes, fluorotelomerization and electrochemical fluorination, to produce AFFFs (Schultz, Barofsky, and Field, 2004a; 2004b). These different processes produce AFFF with unique chemical signatures, which can be useful for source identification and differentiation:

- The electrochemical fluorination process produces mixtures of linear and branched chains with both odd and even numbers of fluorinated carbons (Schultz, Barofsky, and Field, 2004a); and
- The fluorotelomerization process yields products that have linear homologous fluoroalkyl chains and contain only even numbers of fluorinated carbons (Lindstrom, Strynar, and Libelo, 2011), although odd numbers of carbon may be formed through natural biotransformation processes (Liu et al., 2010).

Experts consider the use of AFFF for firefighting training and emergency response to be one of the most common sources of PFAS released to the environment. AFFF is typically applied repeatedly during firefighting training and has been discharged to the ground surface over several decades, often without full

THERE ARE THREE TYPES OF AFFF PRODUCTS THAT CONTAIN PFAS:

(ITRC, 2018)

З

1 Legacy perfluorooctane sulfonic acid (PFOS) AFFF: These foams contain PFOS and precursors that could potentially transform to PFOS (Backe, Day, and Field, 2013). 3M manufactured these exclusively in the U.S. from the late 1960s until 2002 and sold them with the brand name Light Water (DoD, 2014).

2 Legacy fluorotelomer AFFF: U.S. manufacturers produced these foams which contain 50% to 98% short-chain (<C6) PFAS and a remaining balance of long-chain PFAS—from the 1970s until 2016. (Weiner et al., 2013). These foams include all brands of AFFF except Light Water (Schultz, Barofsky, and Field, 2004).

Modern fluorotelomer AFFF: These foams contain short-chain (<C6) PFAS, which scientists consider lower in toxicity and to have significantly reduced bioaccumulation potential compared to long-chain PFAS. Most of the AFFF manufacturers have transitioned to producing short-chain fluorotelomer-based PFAS in response to the U.S. Environmental Protection Agency's (EPA) voluntary perfluorooctanoic acid (PFOA) Stewardship Program, which eliminated all PFOA production and product content by 2015 (EPA, 2016).

connect 🗹 📑

HALEY & ALDRICH TECHNICAL UPDATE: AFFF for firefighting

containment or wastewater management (Bell et al., 2019). Firefighting training areas typically consist of paved or unpaved areas where fuel-based fires are set.

The fires are extinguished by applying AFFF during firefighting training exercises or emergency responses. Waste firefighting water containing residual fuels and AFFF are often conveyed via unlined site drainage ditches to basic effluent treatment centers primarily designed to remove hydrocarbons (but not PFAS) and are then discharged to third-party wastewater treatment plants, surface water, or groundwater via

References cited

Backe, Will J., Thomas C. Day, and Jennifer A. Field. 2013. "Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS." Environmental Science & Technology 47 (10): 5226-34. <u>https://doi.org/10.1021/es3034999</u>.

Bell, Caitlin H., Margaret Gentile, Erica Kalve, Ian Ross, John Horst, Suthan Suthersan, et al. 2019. Emerging Contaminants Handbook. CRC Press. <u>https://doi.org/10.1201/b22226</u>.

Department of Defense. 2014. "Chemical & Material Emerging Risk Alert. Aqueous Film Forming Foam. Risk Alert #03-11." 2014. <u>https://www.denix.osd.mil/cmrmp/ecmr/ecprogrambasics/</u> resources/chemical-material-emerging-risk-alert-for-afff.

Filipovic, Marko, Andreas Woldegiorgis, Karin Norström, Momina Bibi, Maria Lindberg, and Ann-Helen Österäs. 2015. "Historical Usage of Aqueous Film Forming Foam: A Case Study of the Widespread Distribution of Perfluoroalkyl Acids from a Military Airport to Groundwater, Lakes, Soils and Fish." Chemosphere, Per- and Polyfluorinated Alkyl substances (PFASs) in materials, humans, and the environment - current knowledge and scientific gaps., 129 (June): 39-45.

Interstate Technology & Regulatory Council. 2018. "ITRC 2018. PFAS Fact Sheets. Aqueous Film-Forming Foam (AFFF)."

Lindstrom, Andrew B., Mark J. Strynar, and E. Laurence Libelo. 2011. "Polyfluorinated Compounds: Past, Present, and Future." Environmental Science & Technology 45 (19): 7954-61. https://doi.org/10.1021/es2011622.

Liu, Jinxia, Ning Wang, Bogdan Szostek, Robert C. Buck, Patricia K. Panciroli, Patrick W. Folsom, Lisa M. Sulecki, and Cheryl A. Bellin. 2010. "6-2 Fluorotelomer Alcohol Aerobic Biodegradation in Soil and Mixed Bacterial Culture." Chemosphere 78 (4): 437-44. https://doi.org/10.1016/j.chemosphere.2009.10.044. percolation pits (Bell et al., 2019). Such practices, as well as the incomplete capture of fire suppression fluids within the firefighting training area, stormwater runoff, and/or leaks through cracks in concrete pads and associated drainages, have resulted in releases of PFAS to the environment (Bell et al., 2019). As a result, PFAS are often found within shallow surface soils as well as groundwater and surface water around and beneath firefighting training areas (Weber et al., 2017) and other locations where Class B fires have been suppressed using synthetic firefighting foam (Filipovic et al. 2015).

Moody, Cheryl A., and Jennifer A. Field. 2000. "Perfluorinated Surfactants and the Environmental Implications of Their Use in Fire-Fighting Foams." Environmental Science & Technology 34 (18): 3864–70. https://doi.org/10.1021/es991359u.

Schultz, Melissa M., Douglas F. Barofsky, and Jennifer A. Field. 2004a. "Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS." Environmental Science & Technology 38 (6): 1828–35. https://doi.org/10.1021/es035031j.

Schultz, Melissa M., Douglas F. Barofsky, and Jennifer A. Field. 2004b. "Fluorinated Alkyl Surfactants." Research-article. Https://Home.Liebertpub.Com/Ees. July 6, 2004. https://doi.org/10.1089/109287503768335959.

US Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention. 2016. "Fact Sheet: 2010/2015 PFOA Stewardship Program." Collections and Lists. EPA. May 10, 2016. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program.

Weber, Andrea K., Larry B. Barber, Denis R. LeBlanc, Elsie M. Sunderland, and Chad D. Vecitis. 2017. "Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts." Environmental Science & Technology 51 (8): 4269-79. <u>https://doi.org/10.1021/acs.est.6b05573</u>.

Weiner, Barbara, Leo Yeung, Erin B. Marchington, Lisa A. D'Agostino, and Scott A. Mabury. 2013. "Organic Fluorine Content in Aqueous Film Forming Foams (AFFFs) and Biodegradation of the Foam Component 6: 2 Fluorotelomermercaptoalkylamido Sulfonate (6: 2 FTSAS)." In. <u>https://doi.org/10.1071/en13128</u>.

TIMELINE

PFAS PRODUCTION AND USE

1947

3M starts mass-manufacturing PFOA, one of the best-known members in a family of thousands of fluorochemicals called PFAS.

1953

A close relative of PFOA – PFOS – is used in textiles, as it repels oil and water.

1970s

Worldwide military sites, civilian airports, and firefighting training centers start using AFFF.

2006

EPA launches the PFOA Stewardship Program with the goal of eliminating PFOA and precursors from emissions and products by 2015.

1951

DuPont starts using PFOA to make Teflon™.

1968

3M and the U.S. Navy develop "aqueous filmforming foam," firefighting foam containing PFOS and PFOA.

2000

3M announces it will voluntarily halt production of PFOS and PFOA and will stop putting them in products by 2002.

2015

All participating companies state that they have met the PFOA Stewardship Program's goal of eliminating PFOA and precursors from emissions and products by 2015.

For more information, contact us at:

John Xiong, Ph.D., P.E.

Emerging Contaminants Practice Leader Tel: (714) 371.1808 jxiong@haleyaldrich.com

Anita Broughton

General Manufacturing Market Segment Leader Tel: (619) 285.7104 abroughton@haleyaldrich.com

Michael Basel

Aerospace Market Segment Leader Tel: (913) 693.1901 mbasel@haleyaldrich.com