

# Commonwealth of Massachusetts Executive Office of Energy & Environmental Affairs

# Department of Environmental Protection

One Winter Street Boston, MA 02108 • 617-292-5500

Charles D. Baker Governor

Karyn E. Polito Lieutenant Governor Kathleen A. Theoharides Secretary

Martin Suuberg Commissioner

To: Gary Moran, Deputy Commissioner of Operations, MassDEP

Paul Locke, Division Director Bureau of Waste Site Cleanup, MassDEP

From: Nicholas Child, Chief Emergency Planning & Preparedness Officer, MassDEP

Re: Summary of the MassDEP/CTDEEP sampling analysis of select "fluorine-free" foams

**Date:** August 19, 2021

Massachusetts Department of Environmental Protection (MassDEP), in partnership with the Connecticut Department of Energy and Environmental Protection (CTDEEP) and fire service in both states, has conducted a study involving the analysis of six aqueous film-forming foams (AFFF) currently on the market and listed as "fluorine-free". Off-the-shelf foams were acquired by CTDEEP and provided to MassDEP's contract laboratory Alpha Analytical Laboratories, Inc. for PFAS analyses. Additional analyses, not specific to PFAS, were also conducted by Alpha Analytical Laboratories, Inc., Harvard University and Sterling Analytical, Inc.

The purpose of this document is to summarize the results of the study. The full analytical reports are available upon request.

#### Methodology

The subject foams were selected based on the following criteria:

- 1) Meet the National Fire Protection Association (NFPA) 11 standard for low-, medium-, and high-expansion foams.
- 2) Meet Underwriter Laboratory (UL) 162 of approved foams.
- 3) Can be used with current fire department foam equipment.
- 4) Can be applied to both polar and non-polar flammable liquid fires.

The following analytical methods were employed in this study.

#### PFAS by LC-MS/MS with Isotope Dilution (Alpha Analytical)

This method quantifies the concentration of specific PFAS compounds in a sample using a liquid chromatography tandem mass spectrometry method (LC/MS/MS) with solid phase extraction. The approach incorporates extracted internal standards, consisting of (19) <sup>13</sup>C –enriched and (2) <sup>2</sup>H-enriched compounds.

## • Total Oxidizable Precursors Assay, aka TOP Assay (Alpha Analytical)

This method is designed to identify and quantify PFAS precursors present in a sample that would not otherwise be measured by the PFAS by LC/MS/MS analysis. The TOP assay is an analysis by difference approach, where two portions of a sample are analyzed, before-and-after exposure to strong oxidizing conditions (treatment). The PFAS concentration difference between the pre- and post-treatment samples is defined as the amount of oxidizable precursors present in the sample. (In the table below, the pre-treatment and post-treatment results are reported in separate columns.)

# Semi Volatile organics by GC/MS EPA 8270 (Alpha Analytical)

This method is designed to identify and quantify semi-volatile organic compounds ("SVOCs") in a sample. These are compounds that have relatively high molecular weight and high boiling point temperatures. Common SVOCs that could be identified using this method include Polycyclic Aromatic Hydrocarbons ("PAHs", such as benzo[a]pyrene, naphthalene and anthracene), Polychlorinated biphenyls (PCBs), and numerous pesticides (such as DDT, aldrin and parathion.) This method does <u>not</u> detect PFAS compounds.

### Total inorganic halides by ion chromatography (Harvard University)

This method is designed to identify and quantify the halides present in a sample. Halides are compounds that are a combination of a metal and one of the five halogen elements (chlorine, bromine, fluorine, iodine, and astatine). One example of a halide compound is common salt, or sodium chloride (NaCl). In this study, the presence of fluorides (F) are of particular interest.

# Total halogens by combustion ion chromatography (Harvard University)

This method also identifies and quantifies the halides present in a sample following high temperature pyrolysis (breakdown of compounds in the absence of oxygen.)

 Total organic halogens SW846 Method 9076 and Total organic halogens SW846 Method 9023 (Sterling Analytical)

These methods are designed to identify and quantify the organic halides present in a sample. Organic halides are organic compounds containing a halogen atom bonded to a carbon (C) atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) are all types of halogen atoms. For example, a compound that contains an carbon atom bonded to a fluorine atom (C–F) is called an organofluoride.

#### Results

The results are summarized below and color-coded based on analytical results.

|                              | AlphaLabs   | Alpha Labs  | Alpha Labs  | Alpha Labs                                      | Harvard U.                                    | Harvard U.                                      | Sterling Analytical  |
|------------------------------|---|---|---|---|---|---|--|
|                              | PFAS by Isotope<br>Dilution                                 | Total Oxidizable<br>Preursor (TOP)<br>Assay (Pre-<br>Treatment) | TOPAssay (Post -<br>Treatment)  | Semivolatile<br>Organics by GC/MS<br>(EPA 8270) | Inorganic<br>halides by ion<br>chromatography | Total halogens by combustion ion chromatography | Total organic halogens/extractable halides (Detection Limit: 50 ppm)       |
| Universal<br>Green AR        | Non-Detect  | Non-Detect  | Non-Detect  | Non-Detect                                      | Non-Detect                                    | Non-Detect                                      | Non-detect<br>(NOTE: SW-846 Method<br>9076, Total organic<br>halogens)     |
| PhosChek<br>Fluorine<br>Free | Non-Detect  | Non-Detect  | Non-Detect  | Non-Detect                                      | Non-Detect                                    | Cl  | Non-detect<br>(NOTE: SW-846 Method<br>9076, Total organic<br>halogens)     |
| Nova Cool                    | PFHxDA (J)  | Non-Detect  | PFBA<br>PFPeA (J)<br>PFHxA (J)  | Not analyzed                                    | F, Cl   | Non-detected<br>(Cl not quantified)<br>***      | Non-detect<br>(NOTE: SW-846 Method<br>9076, Total organic<br>halogens)     |
| Knockdown                    | PFHxA (J) *<br>field blank                                  | PFHxA (J) *<br>detected in<br>method blank                      | PFBA (J) * detected in method blank  PFHxA (J) * detected in method  PFHpA(J) | Not analyzed                                    | Cl **   | Non-Detect                                      | Non-detect (NOTE: SW-846 Method 9023, Extractable organic halides)         |
| F-500                        | PFHxA (J) *<br>field and method<br>blank                    | PFHxA (J) *   | PFBA (J) * PFPeA (J) PFHxA (J)* PFHpA (J)                                     | Not analyzed                                    | Non-Detect                                    | Non-Detect                                      | Non-detect<br>(NOTE: SW-846 Method<br>9023, Extractable organc<br>halides) |
| Firestopper XL<br>Plus FFC   | PFBA PFPeA 4:2 FTS PFHxA 8:2 FTS(F) 6:2 FTS (dupe) 10:2 FTS | PFBA, 6:2FTS<br>PFHxA   | Non-detect ***<br>Reporting limits<br>very high                               | Non-Detect                                      | CI **   | F, Cl   | Non-detect<br>(NOTE: SW-846 Method<br>9076, Total organic<br>halogens)     |

<sup>\*</sup> Also found with J-value in field and/or method blank analysis.

Note 1 - J-values are above the detection limit, but below the reporting limit for the analysis. This means that there is a high degree of certainty that PFASare present in the sample, but the quantitative concentration values are uncertain.

Note 2- Knock Down and Fire Stopper had detects of chlorine (CI) in the Harvard analysis for inorganic halides. Since similar results were detected in the temperature blank, the result is likely to be a false positive.

Note 3 - The results from Sterling Analytical are not inconsistent with those from other analyses due to high detection limits.

# **Conclusions**

Based on the analysis, one advertised Fluorine Free Foams (Universal Green AR) had no detects for fluorinated or other halogenated compounds. Four advertised Fluorine Free Foams PhosCheck Fluorine Free, NovaCool, Knockdown, and F-500 did show very low levels of fluorine and/or other halogens. As stated by Alpha Analytical, detection at these levels is extremely difficult and the possibility of other non-foam concentrate sources as well as sampling methodology shade the results. One foam, FireStopperXL Plus FFC did show several PFAS compounds and should not be considered a comparable Fluorine Free Foam. The analytical reports will be posted on the MassDEP BWSC PFAS web page shortly<sup>1</sup>.

At this time, the workgroup is not considering analysis of any other fluorine free foam concentrates. Readers may also consider the analytical work being performed by the Green Screen project<sup>2</sup>.

<sup>\*\*</sup> Also found in temperature blank at similar concentration.

<sup>&</sup>lt;sup>1</sup> https://www.mass.gov/info-details/per-and-polyfluoroalkyl-substances-pfas

https://www.greenscreenchemicals.org/certified/fff-standard