UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON D.C., 20460

OFFICE of CHEMICAL SAFETY AND POLLUTION PREVENTION
OFFICE of PESTICIDE PROGRAMS

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MEMORANDUM

SUBJECT: Results of EPA's Analytical Chemistry Branch Laboratory Study of PFAS Leaching from Fluorinated HDPE Containers.
ACB Project B21-02

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BACKGROUND and SUMMARY

In March 2021, the Agency released data on a study titled "Rinses From Selected Fluorinated and Non-Fluorinated HDPE Containers". Based on that study, the Analytical Chemistry Branch (ACB) concluded that tested fluorinated high density polyethylene (HDPE) containers have certain perfluorinated alkyl substances (PFAS) on/in their walls, and that those PFAS compounds can leach into the liquid products (mosquito control products) stored in those containers.

In this current study, the ACB tested the impact of other variables - specifically the length of time a pesticide product is stored in fluorinated and non-fluorinated polyethylene containers, and the different types of liquid (such as water and methanol) used in the product - on the leaching potential of PFAS. Thirty-one (31) PFAS compounds (see **Attachment I**) were targeted in this study, using a modified EPA Method 537.1 . This study was not designed to provide any quantitative data for assessing risk of PFAS leaching from fluorinated HDPE containers into the liquid products that stored in such containers.

ACB purchased several brands of clean/never used before fluorinated and non-fluorinated containers from the open market in the spring and summer of 2021. These fluorinated and non-fluorinated containers were tested at different time intervals (up to twenty weeks) for simulated stored products containing methanol or water. Results show that in all fluorinated containers tested, higher levels of total PFAS were found in the methanol (up to ~ 15 ppb) and water (up to ~3 ppb) leachates compared to that from non-fluorinated container leachate, whereas the highest total level of PFAS found is about 0.04 ppb, which is similar to the laboratory background levels commonly encountered.

STUDY DESIGN

The ACB conducted a study to evaluate the leaching potential of PFAS from fluorinated container walls into simulated liquid pesticide products stored in these containers. Most of the liquid pesticide products are formulated aqueous solutions with surfactants, and some products are formulated with organic solutions (e.g., oil, organic solvents). Water and methanol were chosen in this study to represent the latter types of products, with water being the weakest solution and methanol representing the strongest solution that can leach PFAS from the container walls. Aqueous solutions with surfactants should have stronger ability than water alone, because of the hydrophobicity properties of the surfactants, in leaching PFAS from container walls.

Three different brands of fluorinated polyethylene containers were used (see **Table 1**). For Brand B and Brand C, two containers each were filled to capacity, one with high purity water, one with methanol, and used for the entire length of the study. For Brand A, due to small container size, two containers (one for water, one for methanol) were used for each time point. All containers were left on the counter in a laboratory away from direct sunlight at room temperature. An aliquot of the solutions (200 ml) was taken at each time point from each container. The aliquots, either water or methanol, were processed and analyzed for presence of thirty-one PFAS compounds (see Appendix I), using the same modified EPA Method 537.1, as described in the Agency's March 2021 data release. The methanol samples were concentrated and reconstituted to 1 ml of final solutions and then analyzed using the same instrumental method as for the water samples. Procedural blanks and fortified blanks were used at each sampling period as analytical quality controls.

Non-fluorinated HDPE containers were also filled with water or methanol and aliquots of the solutions were taken and analyzed at the same time along with those from the fluorinated containers for comparison.

Table 1. HDPE containers used in the leaching study and the sampling scheme.

Containers tested	Leaching solution	Sampling period after filling up with liquid (one sample at each time point)
Brand A, nonfluorinated 250 ml HDPE	Water, 1 bottle per time point	1 day, 1 week, 4 weeks, 10 weeks, 20 weeks
	Methanol, 1 bottle per time point	
Brand A, fluorinated 250 ml FLPE *	Water, 1 bottle per time point	1 day, 1 week, 4 weeks, 10 weeks, 20 weeks
	Methanol, 1 bottle per time point	
Brand B, fluorinated 1 gal HDPE	Water, 1 piece	1 day, 1 week, 4 weeks, 10 weeks, 20 weeks
	Methanol, 1 piece	
Brand C, fluorinated 2.5 gal HDPE	Water, 1 piece Methanol, 1 piece	1 day, 1 week, 4 weeks, 10 weeks, 20 weeks

* FLPE: Fluorinated High Density Polyethylene. The fluorination technology or fluorination degrees of these containers are unknown.

RESULTS

Eight out of the thirty-one PFAS compounds that were targeted in the analytical method were positively identified in the water and methanol samples of all the fluorinated containers and are listed in **Table 2**. These same eight compounds were also identified in the ACB March 2021 rinse study.

Table 2. List of PFAS compounds that were positively identified in the leachates of the fluorinated HDPE containers.

Abbreviated name	***Full name***
PFBA	*Perfluoro-butanoic acid*
PFPeA	*Perfluoro-pentanoic acid*
PFHxA	*Perfluoro-hexanoic acid*
PFHpA	*Perfluoro-heptanoic acid*
PFOA	*Perfluoro-octanoic acid*
PFNA	*Perfluoro-nananoic acid*
PFDA	*Perfluoro-decanoic acid*
PFUdA	*Perfluoro-undecanoic acid*

The summation (total of the concentrations) of the eight identified PFAS compounds in the water and methanol leachates are listed in **Tables 3 and 4**, respectively. The values are in ng/ml (or ppb) of water or methanol in the containers.

Table 3. Total PFAS concentration (ng/ml of water (ppb), summation of detected PFAS compounds) in water leachates at different storage time points of non-fluorinated and fluorinated containers.

Containers	**1 day**	**1 week**	**4 weeks**	**10 weeks**	**20 weeks**
Brand A, Non-fluorinated	0.003	0.021	0.001	0.002	0.000
Brand A, Fluorinated	0.092	0.335	1.115	2.467	2.888
Brand B, Fluorinated	0.103	0.393	0.391	0.677	0.654
Brand C, Fluorinated	0.016	0.131	0.276	0.697	0.907

Table 4. Total PFAS concentration (ng/ml of methanol (ppb), summation of detected PFAS compounds) in methanol leachates at different storage time points of non-fluorinated and fluorinated containers.

Containers	1 day	1 week	4 weeks	10 weeks	20 weeks
Brand A, Non-fluorinated	0.014	0.009	0.014	0.045	0.022
Brand A, Fluorinated	8.184	6.065	1.238	14.720	4.970
Brand B, Fluorinated	0.977	0.967	1.035	1.541	3.120
Brand C, Fluorinated	1.026	0.614	0.980	1.489	1.896

Figures 1 and 2 are graphic displays of the PFAS levels found in water and methanol leachates from tested containers, with some notable observations

- Water or methanol stored in fluorinated containers have elevated PFAS levels, a clear indication of the migration (leaching) of PFAS from container walls to the liquid solutions in the container.
- The total (summation) amount of leached PFAS at each time point is different for different brands of fluorinated containers, likely a reflection of different fluorination degree and technology of these containers.
- The amount of PFAS leached into the solutions generally increases with time during the 20-week testing period, indicating continued gradual leaching over time.
- Higher amount of PFAS was found in methanol solution (up to 15 ppb total, week 10) than that in water (up to 3 ppb total, week 20) of the same containers, an observation consistent with that of methanol being a stronger solvent in dissolving organic compounds, thus a stronger solution in leaching of PFAS from the HDPE container walls.
- The leaching rate with methanol is much faster than with water as shown by the high PFAS concentrations in the methanol from day one of the tests.
- The highest level of PFAS from the non-fluorinated containers is 0.045 ppb in methanol leachate. This detection is likely derived from laboratory equipment and reagents and is believed to reflect background levels.

Figure 1. Amount of PFAS in water stored in fluorinated HDPE containers over time. A non-fluorinated container was used as comparison.

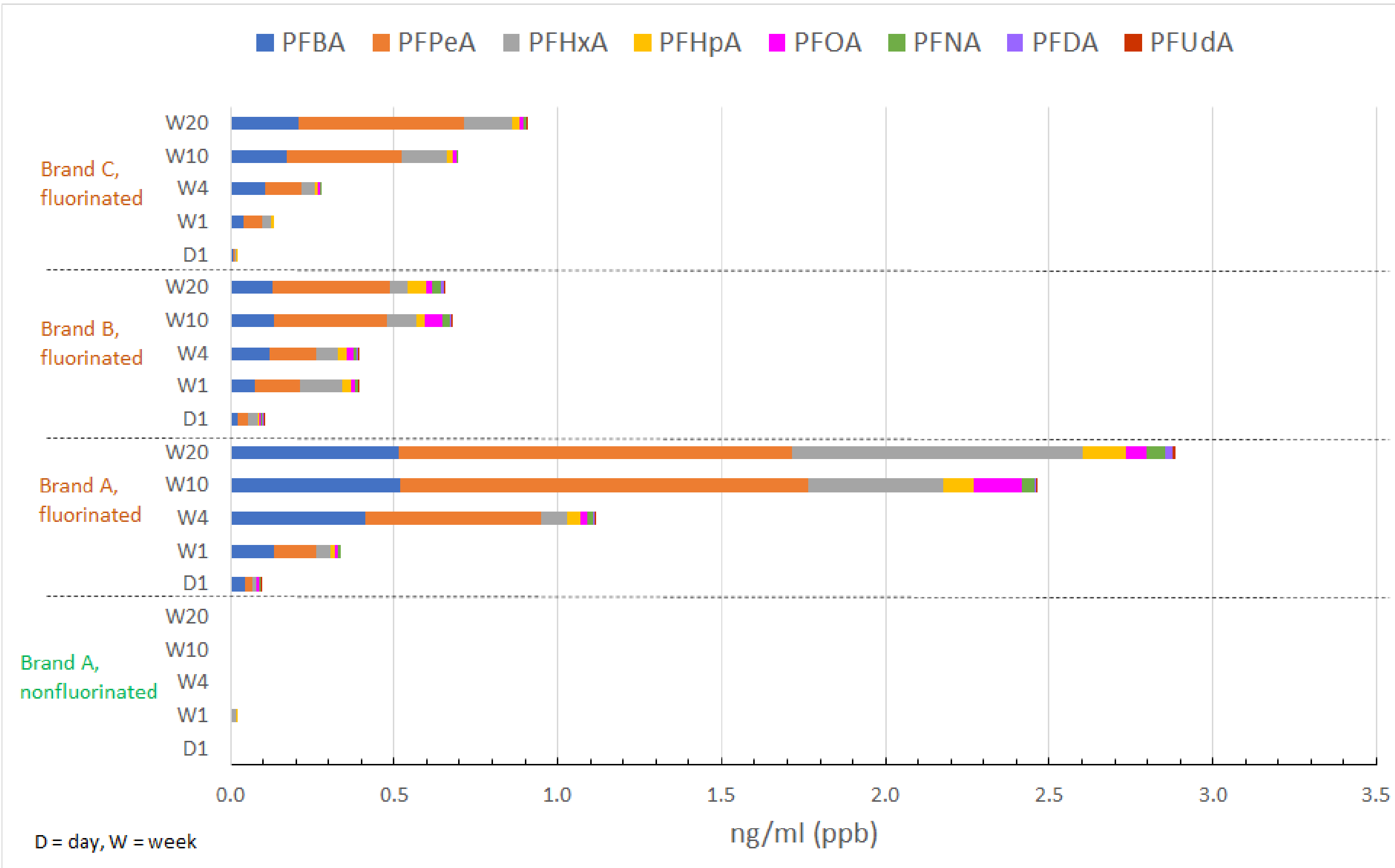
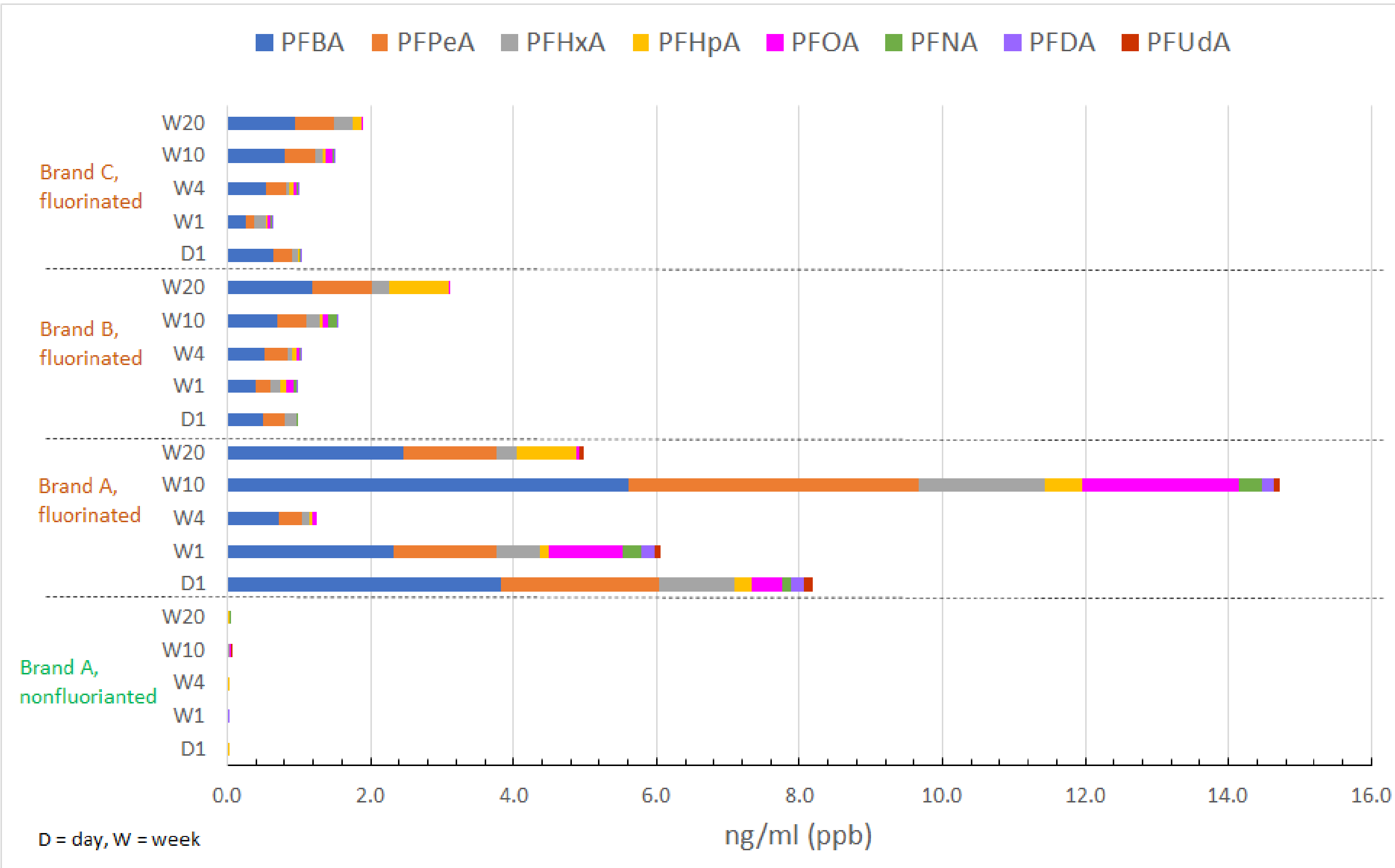


Figure 2. Amount of PFAS in methanol stored in fluorinated HDPE containers over time. A non-fluorinated container was used as comparison. The amount of PFAS leached into methanol from one brand of container, although elevated, showed a random pattern of amount leached over time. Individual containers (250 ml size) were used for each time point and the variations among different container replicates may have contributed to the difference in the leached amount for this brand.



SIGNIFICANCE and LIMITATION OF THE STUDY RESULTS

As demonstrated in previous rinse study (March 2021), PFAS, which were formed as by-products during the fluorination process of HDPE containers, do leach from container walls into the products they contain. This study further demonstrates that the amount of PFAS leached into the products will increase over storage time in these types of fluorinated containers. Furthermore, the stronger the solvent in which the product is formulated, the higher the amount of PFAS leached. The amount of PFAS leached varies with the brands of containers, likely a reflection of different fluorination degree and technology used for each container.

The agency is aware that there are different fluorination technologies for the HDPE containers. Because the tested containers were purchased from open market, the fluorination technologies used for these tested containers are unknown to the agency.   It is unclear at this time if PFAS would be present in all fluorinated containers treated by different fluorination technologies. Additional tests may be needed on fluorinated containers from different fluorination technologies to verify if PFAS would be present in those containers.

Attachment I – Targeted PFAS and their CAS numbers

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ATTACHMENT I - TARGETED PFAS

CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS and CHEMICAL NAMES
PFAS: Per- and polyfluoroalkyl substances

	CAS #	Full Name
PFBA	375-22-4	Perfluorobutanoic Acid
PFBS	375-73-5	Perfluorobutanesulfonic Acid
PFPeA	2706-90-3	Perfluoropentanoic Acid
PFPeS	2706-91-4	Perfluoropentanesulfonic Acid
PFHxA	307-24-4	Perfluorohexanoic Acid
PFHxS	355-46-4	Perfluorohexanesulfonic Acid
PFHpA	375-85-9	Perfluoroheptanoic Acid
PFHpS	375-92-8	Perfluoroheptanesulfonic Acid
PFOA	335-67-1	Perfluorooctanoic Acid
PFOS	1763-23-1	Perfluorooctanesulfonic Acid
PFNA	375-95-1	Perflurononanoic Acid
PFNS	68259-12-1	Perfluorononanesulfonic Acid
PFDA	375-76-2	Perfluorodecanoic Acid
PFDS	335-77-3	Perfluorodecanesulfonic Acid
PFUdA/PFUnA	2058-94-8	Perfluoroundecanoic Acid
PFDoA	307-55-1	Perfluorododecanoic Acid
PFDoS	70780-39-5	Perfluorododecanesulfonic Acid
PFTrDA	72629-94-8	Perfluorotridecanoic Acid
PFTeDA	376-06-7	Perfluorotetradecanoic Acid
PFHxDA	67905-19-5	Perflurohexadecanoic Acid
PFODA	16517-11-6	Perfluorooctadecanoic Acid
4:2 FTS	27619-93-8	Perfluorohexane sulfonate (4:2)
6:2 FTS	27619-94-9	Perfluorooctane sulfonate (6:2)
8:2 FTS	27619-96-1	Perfluorodecane sulfonate (8:2)
FOSAA	2806-24-8	Perfluorooctane sulfonamidoacetic Acid
N-MeFOSAA	2355-31-9	N-Methyl Perfluorooctane sulfonoamidoacetic Acid
N-EtFOSAA	2991-50-6	N-Ethyl Perfluorooctane sulfonoamidoacetic Acid
HFPO-DA	13252-13-6	GenX; 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
NaDONA	958445-44-8	Sodium dodecafluoro-3H-4,8-dioxanonanoate
9Cl-PF3ONS	73606-19-6	Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate
11Cl-PF3OUdS	83329-89-9	Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate