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

OFFICE OF
CHEMICAL SAFETY AND
POLLUTION PREVENTION

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MEMORANDUM

SUBJECT: EPA's Analytical Chemistry Branch PFAS Testing
Rinses from Selected Fluorinated and Non-Fluorinated HDPE Containers

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BACKGROUND

The EPA's Analytical Chemistry Laboratory at Fort Meade has tested a limited number of fluorinated and non-fluorinated HDPE (High Density Polyethylene) containers for presence of PFAS (Per- and Polyfluoroalkyl Substances). This effort is in support of the Agency's investigation on the source(s) of PFAS found in a mosquito control pesticide product. This memorandum summarizes our findings and discusses the limitations of the results.

The EPA also tested a limited number of samples of a mosquito control pesticide product collected at different steps in the production and manufacturing of that product, the final results of which will be reported in a separate memorandum (after review by our Quality Assurance Officer (QAO) for compliance with the ISO-17025 guidelines). Preliminary results of this analysis are discussed briefly in this memorandum in terms of their overall trend.

SUMMARY OF RESULTS

The data included in this report represent results from testing the following HDPE container samples, which are submitted by the producer of the pesticide product. All fluorinated containers were of the same fluorination level (Level 3), which is specific to the manufacturer:

- One (1) fluorinated HDPE 2.5-gallon jug that previously contained the product (used)
  (Two jugs were received, of which one was analyzed.)
- Two (2) fluorinated HDPE 2.5-gallon jugs that never contained the product (unused)
- Two (2) fluorinated HDPE 55-gallon drums that never contained the product (unused)
- Two (2) fluorinated HDPE 30-gallon drums that never contained the product (unused)
- Two (2) non-fluorinated HDPE 2.5-gallon jugs that never contained the product (unused)

The EPA performed a rinse procedure on the containers and analyzed the rinsates using the modified EPA Method 537.1[1]. The following PFAS compounds were positively identified:

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 total level of all PFAS found in the rinsates of the fluorinated HDPE containers ranges from 20 - 50 ppb, while 1 ppb or less was detected in the non-fluorinated containers.

Attachment I.1 lists the PFAS that were targeted in this study. A summary of the results is provided in **Attachment I.2**. Procedures for collecting the rinsate samples from the containers are included in **Attachment I.3**. Pictures of the containers are shown in **Attachment I.4**.

DISCUSSION

Results of the Rinse Samples (Rinsates)

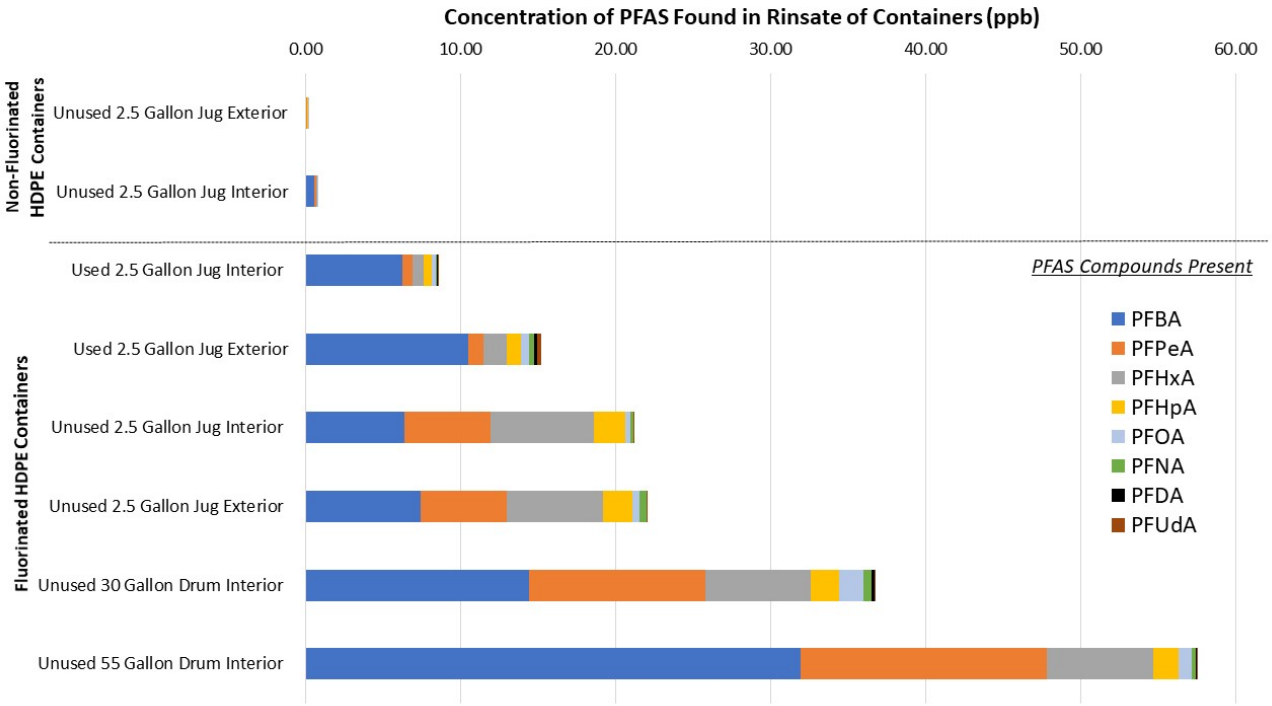
All containers received were analyzed, except for one used 2.5-gallon jug. Due to time limitation of this study, each container was rinsed once for analysis.

The 2.5-gallon jugs were rinsed inside and outside once with 50 ml of methanol each, and the inside rinsate and outside rinsate were analyzed separately, as stated in **Attachment I.3**. The drums were rinsed inside with 300 ml of methanol, 50 ml of which were used in the analysis. Contact time between the solvent and the walls of the containers was approximately one minute.

Results are reported as averages of measurements from all containers of the same type and size, where applicable. The PFAS compounds detected are comparable between each type of fluorinated container (used and unused). Wide variation between the reported PFAS concentrations is noted with the drums, resulting in relative percent deviation (RPD) greater than 50%, when average values are reported. This could be attributed to the variability in the structure of each drum and in the single-rinse procedure that the laboratory used to collect the rinsates. Less variation is seen with the smaller size container (2.5-gallon jug), with %RPD averaging around 20%.

Figure 1 shows the average level of PFAS in the rinsates from the non-fluorinated HDPE (top) and the fluorinated HDPE (bottom) containers and indicates that PFAS compounds are more abundant in the fluorinated containers than in the non-fluorinated containers.

Figure 1 - Levels of PFAS in rinsates from containers



Preliminary Results of the Product Samples

The final results of analysis of the product samples are not quantified in this memorandum, but will be reported in a separate memorandum, after a full QAO review. Preliminary analysis shows a noticeable difference in the level and the number of PFAS compounds detected in samples of products previously stored in the fluorinated containers (estimated total of 0.2 ppb), versus the product sample collected directly from the production line, which had never been stored in a fluorinated container (approximately 5 times lower level of PFAS compounds detected).

CONCLUSION and NEXT STEPS

Based on the results of the rinsate samples as described above and the preliminary results of the product samples (for which results will be reported in a different memorandum), the EPA believes that through the fluorination process of HDPE containers, PFAS compounds may be formed and then partly leach into the products inside the containers. Based on information given to us by a company that performs fluorination on plastic containers, during the fluorination process, HDPE containers are subjected to fluorine elemental gas at pre-determined concentrations and under elevated temperatures. The anticipated chemical reaction results in formation of partially fluorinated long chain polymers and possibly fully

fluorinated short chain polymers. Similarly, when a mixture of fluorine and oxygen is used during fluorination, oxy-fluorinated polymers are formed. If short chain polyethylene compounds (either impurities/by-products in the manufacturing of HDPE containers or from the degradation of HDPE during fluorination) are present during fluorination, further chemical reaction could occur and transform the oxy-fluorinated polymers into the perfluorinated carboxylic acids, such as the ones detected in this study.

The EPA believes the length of time and the conditions under which the product is stored in the fluorinated containers could affect the leaching potential, and consequently the concentration of PFAS found in the products. Additional studies are needed to determine under what conditions, generally, PFAS compounds will leach from plastic containers into the pesticide products.

The EPA is also planning to conduct additional studies on other types of fluorinated HDPE containers from additional producers. Future studies will test these materials under a variety of different testing conditions, such as: using solvents other than methanol, different contact times for the rinsates, different testing temperatures, and where applicable, different pesticide storage time in fluorinated containers, to better understand what impact fluorination has on plastic containers and the pesticides products they contain.

LIMITATIONS OF THE RESULTS

Please note the following:

1. The intention of this study was to determine potential source(s) of PFAS in a particular mosquito product. While quantitative results were reported, there are many areas of uncertainty in the measurement of the data, including our rinsate sampling procedure. A 50 ml volume of methanol was used for the 2.5-gallon jug versus 300 ml for the drums (30- and 55-gallon). Although the results were normalized to ppb (ng of PFAS compound per ml of rinsate) for ease and uniformity of reporting, comparison of the reported concentration of PFAS between the different sizes of containers should not made.

2. Most of the results of PFAS found in the rinsate samples exceed the highest calibration point of the instrument calibration curve (equivalent to 0.2 ppb). The results reported were estimated by extrapolating beyond the instrument calibration curve. To date, sample dilution was not conducted to accurately determine the concentrations; therefore, these expedited results should not be considered as absolutely quantitative.

ATTACHMENT I

1. Chemical Names and CAS Numbers
2. Results of Rinse Samples
3. Procedures for Collecting Rinses Samples
4. Pictures of Tested Containers

Attachment I.1 -

Chemical Names and CAS Numbers

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		Perfluorohexane sulfonate (4:2)
6:2 FTS		Perfluorooctane sulfonate (6:2)
8:2 FTS		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

Attachment I.2 -

Results of Rinse Samples (Rinsates)

Values presented are ng/ml (ppb) of individual PFAS compound found in the rinsate solution following one rinse with methanol

Date Recevied	11/20/2020			12/21/2020		12/29/2020	12/29/2020	12/29/2020		12/29/2020	
Date Analyzed	[1] 12/7/2020			12/22/2020		12/30/2020	12/30/2020	12/30/2020		12/30/2020	12/30/2020
	Fluorinated Containers			Fluorinated Containers		Fluorinated Containers	Fluorinated Containers	Non-fluorinated containers			
	[2] Used 2.5-gallon Jug			[2] Unused 2.5-gallon Jug		[3] Unused 55-gallon Drum	[3] Unused 30-gallon Drum	[2] Unused 2.5-gallon Jug		[4] Cap Seal	
PFAS compound	Exterior	Interior	*Spike Recovery*	Exterior	Interior	Interior	Interior	Exterior	Interior		*Spike Recovery*
PFBA	10.52	6.27	*0%*	7.43	6.40	31.91	14.40	0.06	0.59	-	*76%*
PFBS	-	-	*437%*	-	-	-	-	-	-	-	*59%*
PFPeA	1.00	0.66	*49%*	5.59	5.58	15.90	11.37	0.04	0.11	-	*66%*
PFPeS	-	-	*247%*	-	-	-	-	-	-	-	*89%*
PFHxA	1.48	0.71	*208%*	6.15	6.62	6.89	6.85	0.04	0.06	-	*108%*
PFHxS	-	-	*85%*	-	-	-	-	-	-	-	*66%*
PFHpA	0.91	0.53	*93%*	1.93	2.04	1.62	1.78	0.02	0.02	-	*73%*
PFHpS	-	-	*95%*	-	-	-	-	-	-	-	*54%*
PFOA	0.49	0.22	*55%*	0.46	0.30	0.87	1.59	0.01	0.01	-	*86%*
PFOS	-	-	*62%*	-	-	-	-	-	-	-	*57%*
PFNA	0.35	0.11	*61%*	0.45	0.25	0.22	0.54	-	-	-	*88%*
PFNS	-	-	*82%*	-	-	-	-	-	-	-	*64%*
PFDA	0.23	0.06	*54%*	-	-	0.08	0.15	-	-	-	*70%*
PFDS	-	-	*73%*	-	-	-	-	-	-	-	*71%*
PFUdA	0.21	0.02	*93%*	0.08	0.05	0.05	0.09	-	-	-	*56%*
PFDoA	-	-	*86%*	-	-	-	-	-	-	-	*56%*
PFDoS	-	-	*125%*	-	-	-	-	-	-	-	*46%*
PFTrDA	-	-	*86%*	-	-	-	-	-	-	-	*90%*
PFTeDA	-	-	*68%*	-	-	-	-	-	-	-	*56%*
PFHxDA	-	-	*183%*	-	-	-	-	-	-	-	*154%*
PFODA	-	-	*M.I.*	-	-	-	-	-	-	-	*M.I.*
4:2 FTS	-	-	*n.s.*	-	-	-	-	-	-	-	*119%*
6:2 FTS	-	-	*n.s.*	-	-	-	-	-	-	-	*93%*
8:2 FTS	-	-	*n.s.*	-	-	-	-	-	-	-	*79%*
FOSAA	-	-	*n.s.*	-	-	-	-	-	-	-	*79%*
N-MeFOSAA	-	-	*n.s.*	-	-	-	-	-	-	-	*96%*
N-EtFOSAA	-	-	*n.s.*	-	-	-	-	-	-	-	*95%*

[1] - This set of samples were analyzed prior to the upgrade of the analytical instrument to PFAS analysis-compatible plumbing. High background level for some compounds in this set made the determination of their quantities difficult.

[2] - 2.5-gallon jugs were rinsed once with 50 ml of methanol, both interior and exterior. Rinsates were concentrated and analyzed.

[3] - 30-gallon and 55-gallon drums were rinsed once with 300 ml of methanol. 50 ml of the rinsate was concentrated and analyzed in duplicate. Results reported are average.

[4] - Four cap seals (white plastic) were rinsed once with 50 ml of methanol. Two rinsates were combined as one sample. Each sample was concentrated and analyzed separately.

Detection limit (DL) in the rinsate sample is estimated to be in the range of 0.0004 to 0.002 ng/ml for different compounds based on the responses of the lowest calibration standards.
"-" denotes analyzed but not detected at or above the DL.
"n.s. - not spiked.
".M.I." - matrix interference and could not be quantitated.

Procedures for rinsing containers for PFAS analysis

ACB Project B21-02

For used containers – Pre-clean containers with laboratory grade detergent first, then rinse with water. Let the containers air dry, then follow procedures as described below

For new and unused containers - No precleaning is needed. Follow procedures as described below

Procedures

1. Sample Collection

For 2.5-gallon jugs:

To rinse the interior of the container, add 50 ml of methanol to the container. Shake and rotate the container to ensure the methanol covers as much as possible the interior surface for approximately 1 minute. Decant the methanol rinsate into a polypropylene tube.

To rinse the exterior of the container, hold and position the jug over a 200 ml beaker with one corner of the jug pointing directly onto the beaker. Using a laboratory squeeze wash bottle, spray methanol over the exterior surface, from top to bottom. Collect the rinsate in the beaker below. Rotate the jug and repeat the methanol rinse step until about 50 ml of methanol is collected in the beaker. Transfer the methanol rinsate into a polypropylene tube.

For 30-gallon and 55-gallon drums:

To rinse the drums, add 300 ml of methanol to the drum and place the cap back on.

Roll the drum on its side slowly for several turns. Place the drum in upright position, and shake it in different directions several times for approximately 1 minute

Decant the methanol rinsate from the drum into a large beaker. Transfer 50 ml of the rinsate into a polypropylene tube.

2. Sample Preparation and Analysis

Prepare quality control (QC) samples, such as procedural blank and laboratory blank spike (LBS) with 50 ml of methanol in polypropylene tubes.

Add PFAS extraction standard to all the rinsate and QC samples in the polypropylene tubes.

Add spiking standard to the LBS.

Concentrate all the samples to dryness under a stream of N_2 on a water bath (40-50^{o}C). Some of the rinsate may not reach dryness.

Add internal standard to each sample.

Add 1 ml of methanol/water (90/10) to each sample. Vortex each tube for 30 sec.

Transfer an aliquot of the samples into polypropylene LC vials with polyethylene caps.

A nylon syringe filter may be used to filter the samples if the samples are cloudy/viscous.

Sample analysis is performed on a liquid chromatography tandem mass spectrometer (LC/MSMS), following EPA method 537.1 "*Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC/MS/MS)*"

Attachment I.4 -

Containers Pictures

2.5-gallon jug

30-gallon drum

55-gallon drum

All containers (jugs and drums) are made of high density polyethylene (HDPE) plastic