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Memorandum

To: Board of Pesticides Control

From: Pamela J. Bryer, Ph.D. | Pesticides Toxicologist | Maine Board of Pesticides Control

Subject: PFAS Container Contamination Updates

Date: October 21, 2022

Introduction

The board is currently tasked with regulating pesticide containers. This memo serves to answer some of the questions posed by board members at the August 5, 2022 board meeting and the topics range widely. Included in this memo is coverage of EPA's container study which has recently been reported to the public; a discussion of the use of some PFAS to directly coat food containers; a statistic indicating the percentage of the US pesticide container supply that is likely treated with fluorination; the current understanding of how much PFAS is in the US food supply; a review of how many pesticides are considered to be PFAS themselves under Maine's definition; a review of a recent EPA press release on the removal of several ingredients from the list of inerts allowed in pesticides because they are PFAS; and finally, there is mention of a recent paper detailing PFAS contamination of several insecticide products.

EPA Container Study Findings *-how likely is PFAS contamination a product of fluorination?*

Previously, the board has been supplied the results of EPA testing demonstrating *de novo* generation of PFAS in pesticide products due entirely to containerization in fluorinated HDPE plastic containers. The staff at EPA's Fort Meade Laboratory conducted a follow-up study to determine if PFAS would 1) leach into water as well as oily substances and 2) how storage duration affected leaching. In late summer 2022, those data were reported,[1]

The full report released by EPA is included in the board packet. In summary, the basic findings of the report were:

1) oil-based and water-based fluids are both likely to contain PFAS following storage in fluorinated HDPE containers,
2) water-based fluids are likely to contain a significantly lower concentration of PFAS than oily-based fluids (oil-based concentration $\leq$ 15 ppb while the water-based concentration $\leq$ 3 ppb)
3) longer storage times generate greater accumulations of PFAS, up to 20 weeks, a pattern seen in both water- and oil-based fluids.

4) samples from plastic containers that were not fluorinated (the control containers) contained ≤ 0.04 ppb PFAS,
5) the PFAS identified were:

PFBA	PFOA
PFPeA	PFNA
PFHxA	PFDA
PFHpA	PFUdA

EPA explained that manufacturers with information that their products contain quantifiable levels of any PFAS compounds are required under FIFRA 6(a)(2) reporting requirements to submit information to EPA about the contamination of the pesticide products within 30 days. EPA has declared that PFAS found in pesticide products are a "toxicological concern". The quantifiable presence of PFAS triggers 6(a)(2) reporting.

Section 6(a)(2) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) states: "If at any time after the registration of a pesticide the registrant has additional factual information regarding unreasonable adverse effects on the environment of the pesticide, he shall submit such information to the Administrator."

Section 152.50(f)(3) of 40 CFR § 159.152 requires applicants to submit, as part of an application for registration, any factual information of which he is aware regarding unreasonable adverse effects of the pesticide on humans or the environment, which would be required to be reported under section 6(a)(2) if the product were registered.

Information about containers ***-how widespread is the scope of fluorinated containers?***

It is currently understood that approximately 20 to 30% of the plastic containers used for pesticide, fertilizers, adjuvants are fluorinated.[2] Beyond this statistic there is little understanding of patterns of fluorinated container use.

PFAS-contamination in context of food packaging ***-how often does PFAS leaching occur?***

Note: the information on food packaging and FDA is included for two reasons, 1) these data are a window into the potential for the likelihood of movement from a package into its contents and 2) these data represent the larger context of PFAS exposure across our lifetime. This information does not directly bear on container fluorination leaching but it reflects on container-generated PFAS contamination and how federal agencies currently address the topic. As detailed below, some food containers are currently coated with PFAS barriers under FDA authority.

The FDA has been studying PFAS in food since the 1990s. Analytical technology has changed and we are currently able to detect PFAS at much lower concentrations than the initial studies. FDA currently allows the use of many PFAS compounds for food-contact surfaces and food manufacturing equipment. Over the past 20 years, voluntary phase-outs have occurred such that currently PFOA, PFOS, and 6:2 FTOH are no longer used in the US for food-contact uses. FDA is aware of the movement of PFAS into food.

US FDA webpage snippet (available at https://www.fda.gov/food/chemical-contaminants-food/authorized-uses-pfas-food-contact-applications) discussing currently authorized uses of PFAS:

<< Per and Polyfluoroalkyl Substances (PFAS)

Since the 1960s, the FDA has authorized specific PFAS for use in specific food contact applications. Some PFAS are used in cookware, food packaging, and in food processing for their non-stick and grease, oil, and water-resistant properties. To ensure food contact substances are safe for their intended use, the FDA conducts a rigorous scientific review before they are authorized for the market.

PFAS that are authorized for use in contact with food generally fall into four application categories:

- Non-stick cookware: PFAS may be used as a coating to make cookware non-stick.
- Gaskets, O-Rings, and other parts used in food processing equipment: PFAS may be used as a resin in forming certain parts used in food processing equipment that require chemical and physical durability.
- Processing aids: PFAS may be used as processing aids for manufacturing other food contact polymers to reduce build-up on manufacturing equipment.
- Paper/paperboard food packaging: PFAS may be used as grease-proofing agents in fast-food wrappers, microwave popcorn bags, take-out paperboard containers, and pet food bags to prevent oil and grease from foods from leaking through the packaging.

<Take away>
FDA allows companies to use PFAS on food contact surfaces. It regulates specific PFAS for specific uses.

US FDA webpage snippet (available at: https://www.fda.gov/food/chemical-contaminants-food/authorized-uses-pfas-food-contact-applications) discussing PFAS in food:

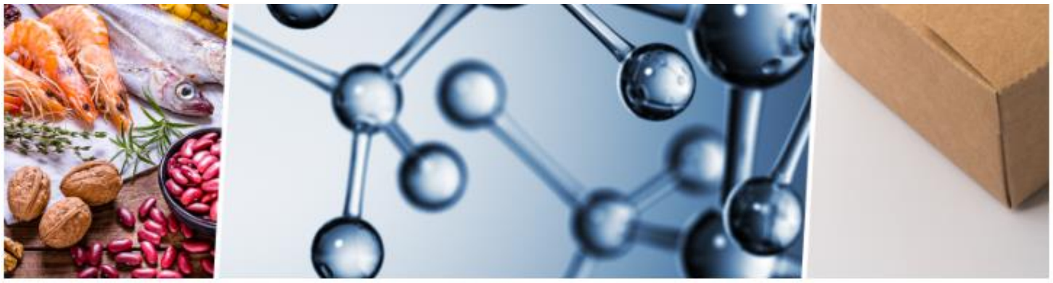
Assessing PFAS Migration Potential from Food Contact Applications

The extent to which PFAS authorized for use in food contact applications migrate to food depends on the molecular structure of the substance, how the final consumer product is manufactured, and its intended use.

- Non-stick cookware: PFAS molecules are polymerized (i.e., joined together to form large molecules) and then applied to the surface of the cookware at very high temperatures, which tightly binds the polymer coating to the cookware. This process vaporizes off virtually all the smaller (i.e., migratable) PFAS molecules. The result is a highly polymerized coating bound to the surface of the cookware. Studies show that this coating contains a negligible amount of PFAS capable of migrating to food.
- Gaskets, O-Rings, and other parts used in food processing equipment: PFAS molecules are polymerized and the resultant large molecules are further joined together (i.e. “crosslinked”) to create a resin that is formed into parts such as sealing gaskets and O-rings, typically used in food processing equipment. This process removes virtually all the smaller (i.e., migratable) PFAS molecules, resulting in a negligible amount of PFAS capable of migrating to food.
- Processing aids: PFAS molecules may or may not be polymerized. However, the amount of PFAS used as processing aids in the manufacture of other food contact polymers is so small that a negligible amount of PFAS is capable of migrating to food from this use.
- Paper and paperboard food packaging: PFAS molecules are not polymerized, but rather are attached to other non-PFAS polymerized molecules as smaller “sidechains” to form the final grease-proofing agent that is applied to the paper packaging. Grease-proofing agents are applied to paper/paperboard packaging at lower temperatures, which are not high enough to remove residual smaller (i.e., migratable) PFAS molecules. Under certain conditions, the smaller PFAS “sidechain” can detach from the polymerized molecule. As a result, there may be potential for PFAS migration to food from this use.

<Take away>
FDA is aware of how much PFAS enters food from these PFAS uses.

US FDA webpage snippet (available at: https://www.fda.gov/food/chemical-contaminants-food/and-polyfluoroalkyl-substances-pfas) on the presence of PFAS in our food supply



Testing Foods & Assessing Safety | Analytical Results | Authorized PFAS | Q&A | Announcements

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of human-made chemicals used in a wide range of consumer and industrial products. PFAS do not easily breakdown and some types have been shown to accumulate in the environment and in our bodies. Exposure to some types PFAS have been linked to serious health effects.

Through the FDA's testing of foods grown or produced in areas with known environmental PFAS contamination, it's clear that PFAS in the soil, water, or air can be absorbed by plants and animals, leading to contaminated foods. However, the FDA's testing of a wide range of foods from the general food supply collected for the Total Diet Study (TDS) has found that overall very few samples have detectable PFAS and those that do, have low levels. In 2022, we conducted a targeted seafood survey and in the limited samples tested we found more types of PFAS and higher levels compared with the fresh and processed foods tested in the TDS samples. We are working to better understand PFAS in seafood, as well as foods in general, to reduce dietary exposure to PFAS that may pose a health concern and will take actions as appropriate to ensure the continued safety of the U.S. food supply.

<Take away>
Only very recently (2019) did FDA start routine sampling for PFAS in their Total Diet Study. Few samples have reported PFAS and they reported low concentrations but there are too few data to draw strong conclusions. FDA commented that without established reference values from EPA it is difficult to know the potential for health effects based on these findings.

PFAS-pesticides in context of all pesticides ***-how many pesticides are PFAS by definition?***

Note: this is repeat information but answers a question from a recent board meeting. In spring 2022, the pesticide product registry database (NSPIRS) was queried to determine how many registered products are likely to be affected by the newer definition of PFAS. This list is subject to change as Maine state agencies further refine the interpretation of the statutory PFAS definition. Each of the 69 actives in this list have some level of fluorination but staff are still seeking input from other agencies for a final determination. BPC does not currently have an official list of PFAS pesticides.

Table 1. List of active ingredient chemistries to be potentially classified as PFAS.

Chemical Name	CAS Number	Number of Registered Products
1-Methyl-3-phenyl-5-(3-(trifluoromethyl)phenyl)-4-pyridone aka fluridone	59756-60-4	8
Acifluorfen-sodium	62476-59-9	1
Benfluralin	1861-40-1	6
Benzovindiflupyr	1072957-71-1	7
Bicyclopyrone	352010-68-5	4
Bifenthrin	82657-04-3	247
Bixafen	581809-46-3	1
Broflanilide	1207727-04-5	4
Bromethalin	63333-35-7	65
Carfentrazone-ethyl	128639-02-1	31
Chlorfenapyr	122453-73-0	8
Cyflufenamid	180409-60-3	1
Cyflumetofen	400882-07-7	2
γ-Cyhalothrin	76703-62-3	24
λ-Cyhalothrin	91465-08-6	127
Dithiopyr	97886-45-8	113
Fipronil	120068-37-3	212
Fluazifop-P-butyl	79241-46-6	43
Fludioxonil	131341-86-1	38
Fluensulfone	318290-98-1	2
Flufenacet	142459-58-3	1
Fluindapyr	1383809-87-7	1
Fluopicolide	239110-15-7	2
Fluopyram	658066-35-4	12
Flupyradifurone	951659-40-8	4
Flurprimidol	56425-91-3	6
Flutolanil	66332-96-5	5
Fluvalinate	69409-94-5	11

Fluxapyroxad	907204-31-3	16
Fomesafen	72178-02-0	4
Fomesafen-sodium	108731-70-0	11
Hexaflumuron	86479-06-3	2
Hydramethylnon	67485-29-4	19
Indoxacarb	173584-44-6	33
Inpyrfluxam	1352994-67-2	2
Lactofen	77501-63-4	1
Mefentrifluconazole	1417782-03-6	6
N-Ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl) benzenamine	55283-68-6	3
Norflurazon	27314-13-2	1
Novaluron	116714-46-6	19
Noviflumuron	121451-02-3	4
Oxathiapiprolin	1003318-67-9	6
Oxyfluorfen	42874-03-3	19
Penoxsulam	219714-96-2	11
Penthiopyrad	183675-82-3	5
Picoxystrobin	117428-22-5	3
Prodiamine	29091-21-2	69
Prosulfuron	94125-34-5	1
Pydiflumetofen	1228284-64-7	9
Pyraflufen-ethyl	129630-19-9	5
Pyrasulfotole	365400-11-9	2
Pyridalyl	179101-81-6	2
Pyrifluquinazon	337458-27-2	2
Pyrimisulfan	221205-90-9	2
Pyroxasulfone	447399-55-5	20
Saflufenacil	372137-35-4	7
Sedaxane	874967-67-6	8
Sulfentrazone	122836-35-5	76
Tefluthrin	79538-32-2	4
Tembotrione	335104-84-2	3
Tetraconazole	112281-77-3	12
Tetraniliprole	1229654-66-3	1
Tiafenacil	1220411-29-9	1
Tralopyril	122454-29-9	66
Trifloxystrobin	141517-21-7	19
Triflumizole	68694-11-1	4
Trifluralin	1582-09-8	28
Triflusulfuron-methyl	126535-15-7	1
	Total products	1,493
	Active Ingredients	69

PFAS-inerts ***-are any inerts that are known to be PFAS?***

In September EPA announced the removal of 12 compounds from the pesticide inerts list due to their chemical structure[3]. EPA allows manufacturers to use any of the compounds off the inerts list in their formulations without additional testing or risk assessment. The inerts list also delineates which compounds may be used on food-use products and which may not. The inerts list is available at: https://www.epa.gov/pesticide-registration/inert-ingredients-overview-and-guidance. Removal of these 12 ingredients does not change the availability or registration of any products in Maine because these 12 compounds were not in use according to EPA records. EPA has previously signaled its desire to "clean up" the inerts list and remove compounds no longer in use and this action is consistent with that intention. When asked, during a call with the states, EPA indicated there are other PFAS compounds still in use. As a reminder, EPA uses a two-carbon chain definition of PFAS that is less restrictive than the state of Maine's definition.

The state of Maine has not previously collected ingredient or formulation information from manufacturers. All compounds not considered to have pesticidal activity are allowed to be kept as confidential business information. Starting with the 2023 registration year Maine will collect that information from registrants during pesticide product renewal and new product registration. Additionally, the legislatively mandated affidavit collection also commences in the 2023 registration year. One affidavit will indicate if a product does or does not contain any PFAS ingredients in accordance with the state's definition. Another affidavit will indicate if a product has been stored in a fluorinated container. The affidavit data will be available in mid-spring of 2023.

PFAS-contamination of pesticides ***-how widespread is PFAS contamination in pesticides?***

A recently published paper identified PFAS compounds in commonly used insecticide products.[4] Researchers found quantifiable PFAS in six out of ten products with one method and seven out of ten products with a secondary method, previously used at a research farm in Texas, see attached paper for details. The one PFAS that was present repeatedly in products at a level of quantification was PFOS. The PFOS had an analytical pattern and was mixed with other certain types of PFAS indicating a specific manufacturing method for the PFOS which has not been allowed in the US for many years. This study also looked at soil, water, and plants grown in the area where the products were used. Soil samples seemed to indicate multiple sources of contamination meaning more than the insecticide use caused the presence of PFOS. The plant samples had several PFAS in them that did not correlate to the PFAS in the insecticides. The authors thought that the PFOS in the plant tissue could come from the insecticides but that there were five additional PFAS present with unknown origins in the plants.

Table 1

Average concentration of PFOS in the analyzed insecticide formulations (mg PFAS/kg formulation or ppm, ± standard deviation). The concentrations reported were calculated from the dilution described previously in the "Insecticide Analysis section". PFAS with no concentrations above LOQ were not included in this table.

Sample ID	Formulation type	Active ingredient	PFOS (mg/kg)
1	Liquid concentrate	Abamectin	3.92 ± 0.51
2	Emulsified suspension	Novaluron	9.18 ± 0.34
3	Liquid concentrate	Mineral Oil (Petroleum oil)	8.64 ± 0.67
4	Emulsified suspension	Imidacloprid	13.3 ± 1.4
5	Emulsified suspension	Spiromesifen	19.2 ± 1.2
6	Liquid concentrate	Malathion	17.8 ± 0.7
7	Wettable powder	*Beauveria Bassiana*	0
8	Wettable powder	Pyridalyl	0
9	Emulsified suspension	Spinosad	0
10	Wettable powder	Spinetoram, Sulfoxaflor	0
BLANK			0

This study is finding PFOS in pesticides at concentrations that are an order of magnitude higher than in previous work with pesticides. Another difference to note, EPA's previous work found eight PFAS compounds adulterating a mosquito insecticide product but did not find reportable levels of PFOS.

Citations

[1] EPA Container Leaching Study available at: https://www.epa.gov/system/files/documents/2022-09/EPA%20PFAS%20Container%20Leaching%20Study%2008122022_0.pdf

[2] Personal communication with M. Hudson, Executive Director of the Ag Container Recycling Council (ACRC) https://www.agrecycling.org/

[3] EPA press release PFAS inert ingredients withdrawn. https://www.epa.gov/newsreleases/epa-proposes-stop-authorized-use-certain-pfas-pesticide-products

[4] Steven Lasee, Kaylin McDermett, Naveen Kumar, Jennifer Guelfo, Paxton Payton, Zhao Yang, Todd A. Anderson. 2022. Targeted analysis and Total Oxidizable Precursor assay of several insecticides for PFAS. Journal of Hazardous Materials Letters 3 (2022) 100067. https://doi.org/10.1016/j.hazl.2022.100067