

Report on the Use of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Pesticides in Maryland 2023

Background

Polyfluoroalkyl substances (PFAS) are a group of manufactured chemicals that have been used in industry and consumer products since the 1940s because of their useful properties. These compounds are synthetic and have multiple fluorine atoms attached to an alkyl chain. There are thousands of different PFAS, some of which have been more widely used and studied than others. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) for example, are two of the most widely used and studied chemicals in the PFAS group. PFOA and PFOS have been replaced in the United States with other PFAS in recent years. One common characteristic of concern of PFAS is that many break down very slowly and can accumulate in humans, animals, plants, and the environment over time (<https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas>).

PFAS can be found in water, soil, air, and food, as well as in households or workplaces. Some examples are drinking water, soil, and water at or near waste sites, fluorinated containers, some pesticide formulations, fire extinguisher foam, biosolids, manufacturing sites that produce or use PFAS, food, food packaging, household products and dust, personal care products, automotive, aviation, aerospace, and defense industries, electronics, cosmetics, medical articles, textiles, and leather. These sources have potential for contaminants to enter the environment, human and animal food chain, as well as humans. Due to their widespread production and use, as well as the ability to be transported and persist in the environment, surveys conducted by the Centers for Disease Control and Prevention (CDC) since 1999 have measured at least 12 PFAS in blood serum. Blood serum was obtained from participants, aged 12 years and older, who have taken part in the National Health and Nutrition Examination Survey (NHANES) published in 2018 (<https://www.cdc.gov/nchs/nhanes/index.htm>).

SB158

The workgroup consists of members from Maryland Department of Health, Maryland Department of the Environment, Maryland Department of Agriculture, and the EPA. Senate Bill 158 tasks the workgroup to study the following:

- An analysis of the health and environmental impacts of PFAS in pesticides in the state

- The identification of testing methods capable of testing for PFAS in pesticides
- An examination of characteristics that distinguish testing methods for PFAS that are validated for drinking water from testing methods that are validated for pesticides
- A status update on federal efforts to certify a method for testing for PFAS in pesticides
- A status update on state and federal efforts to regulate or ban the use of PFAS in pesticides.

The bill tasks Maryland Department of Agriculture to develop a report and present it to the two committees by November 1, 2023.

Pesticide Formulation Summary

To date, the State Chemist Section has 14,029 pesticides and 555 fertilizer-pesticide mixtures registered for distribution in the state of Maryland. These pesticides and fertilizer-pesticides are classified between Section 3 (EPA regulated) and 25b (FIFRA exempt). In both cases the products meet the definition of pesticides provided in the Agricultural Article, Title 5, Subtitle 1, Section 5-101, and Subtitle 2, Section 2-101. Section 5-101 states: “Pesticide” means (1) any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any insects, rodents, fungi, weeds, or other forms of plant or animal life or viruses, except viruses on or in living humans or other animals, which the Secretary declares to be a pest; and (2) any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant. Section 5-102 states: “Pesticide” means any substance or mixture of substances intended for: (1) Preventing, destroying, repelling, or mitigating any pest; (2) Use as a plant regulator, defoliant, or desiccant; or (3) Use as a spray adjuvant such as a wetting agent or adhesive.

The fertilizer-pesticides come in two forms: liquids and granular solids. The fertilizer-pesticides provide nutrients, weed, fungal, and insect control. The liquid forms are weed and feeds that are commonly used on turf and lawns, trees and shrubs, ornamental plants, vegetables, fruit, and gardens. The solids are used for turf and lawns, gardens, trees, and shrubs, and some agricultural applications. The inerts, or in the case of the solid formulations, the fertilizer, provides unique challenges to the analysis of any contaminant or even of the pesticide itself.

The pesticides come in three forms, compressed gasses, solids, and liquids. There are several types of pesticides: algicides, antifoulants, antimicrobials, attractants, biopesticides, biocides, defoliants, desiccants, disinfectants and sanitizers, fungicides, fumigants, herbicides, insect growth regulators, insecticides, miticides, microbial pesticides, molluscicides, ovicides, pheromones, plant growth regulators, plant incorporated protectants, repellents, and rodenticides. Each of these types can be a solid, liquid, gas, or aerosol.

Some examples of solids are pool chemicals (chlorinators and shock treatments), biopesticides (microbial in origin), rodenticides (baits, powders, etc.), insecticide gels (traps, motels, caulk like

treatments, etc.), pet collars (flea and tick for dog and cats), aerosols (insect repellent, insect bombs, yard treatments, etc.), algicides, desiccants (silica gel, and other types of abrasive minerals), agricultural use (solids or liquids to mix into water before applying to a field of crops, or turf grass; and gasses used as fumigants), pass through insecticides used in animal husbandry, and plant incorporated protectants (incorporated into seed stock for planting through gene splicing).

Some examples of gasses are chlorinators (used in water treatment), fumigants (housing and agricultural use), sterilant (food, medical equipment, agricultural uses, etc.), and aerosols (insecticides, repellents, disinfectants, etc.).

Some examples of liquids are pool chemicals (chlorinators and shock treatments), algicides, antifoulants (boat and ship paints), biopesticides (agricultural use, mosquito and insect control, etc.), pet treatments (flea and tick for dogs and cats), yard treatments for insect control, insecticides (forest pest management: spongy moth, emerald ash borer, spotted lantern fly, etc., home treatments, agricultural uses, etc.), herbicides (agricultural, and home use), disinfectants and sanitizers (medical, dental, hospital, home use, etc.), and repellents (insects, and animals). This is not a comprehensive list of what is registered with the State Chemist Section.

Health and Environmental Impacts of PFAS in Pesticides

MDH

PFAS have been linked to adverse dyslipidemia, metabolic syndrome, impaired immune system responses, liver damage, cancer, neurodevelopmental issues, decreasing bone density, reducing antibody response to vaccines, declines in birth weight, reproductive health issues, and certain cancers.^{1,2,3,4} No studies have been identified that specifically address the health impacts of PFAS in pesticides. No studies have been identified that provided exposure models or epidemiologic data that assess the degree to which PFAS in pesticides contribute to human exposure or health effects. However, it is expected that PFAS in pesticides enter environmental waters, vegetation, aquatic and terrestrial life, and air, and contribute to the overall exposure

¹ Fenton SE, Ducatman A, Boobis A, DeWitt JC, Lau C, Ng C, Smith JS, Roberts SM. Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environ Toxicol Chem.* 2021 Mar;40(3):606-630. doi: 10.1002/etc.4890. Epub 2020 Dec 7. PMID: 33017053; PMCID: PMC7906952.

² Sunderland EM, Hu XC, Dassuncao C, Tokranov AK, Wagner CC, Allen JG. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *J Expo Sci Environ Epidemiol.* 2019;29(2):131-147. doi:10.1038/s41370-018-0094-1

³ Brase RA, Mullin EJ, Spink DC. Legacy and emerging per-and polyfluoroalkyl substances: Analytical techniques, environmental fate, and health effects. *Int J Mol Sci.* 2021;22(3):1-30. doi:10.3390/ijms22030995

⁴ Jane L Espartero L, Yamada M, Ford J, Owens G, Prow T, Juhasz A. Health-related toxicity of emerging per- and polyfluoroalkyl substances: Comparison to legacy PFOS and PFOA. *Environ Res.* 2022;212. doi:10.1016/j.envres.2022.113431

burden and associated health impacts in humans. The MDH Laboratory has been running EPA Methods 537.1, 533, and 1633 as an EPA-approved and ISO-accredited laboratory for testing drinking, ground, surface, and waste waters, biosolids, crabs, clams, and fish tissue for the past 3 years and in ongoing partnerships with MDE, DNR, US EPA, and FDA.

MDE

Pesticides containing PFAS compounds have the potential to contaminate soil, surface and groundwater, and air which could result in impacts to aquatic life and human health from direct exposure or the consumption of drinking water and fish. The human health effects are discussed by MDH above. Over the past three years, MDE has extensively monitored fish tissue, drinking water, and surface water in order to characterize PFAS contamination throughout the State in order to address sources of contamination that pose a risk to human health. MDE currently issues fish consumption advisories for PFAS and has identified two water bodies as impaired for PFOS in fish tissue.

MDE has monitored all community water systems throughout the State and is currently working with utilities identified with elevated levels to address PFAS contamination in their drinking water. Additional information can be found on our website: <https://mde.maryland.gov/PublicHealth/Pages/PFAS-Landing-Page.aspx>. However, there is no clear delineation of how much PFAS is related to pesticides or other sources.

Identification of Testing Methods Capable of Testing for PFAS Pesticides

After reviewing available methods, from ASTM, ISO, US EPA, and other official methods, for the analysis of PFAS in environmental, solid waste, human and animal tissue, and other matrices, the common thread among all of them is the instrumentation that is used for the determination of the compounds. Matrices vary from water, both potable and non-potable sources, to more complex matrices as biosolids, tissues, and pesticides. The Maryland Department of Health PFAS Laboratory is EPA-approved and ISO-accredited to run EPA Methods 537.1, 533, and 1633 for PFAS across various matrices including all waters, solids, biosolids, and fish, crab, clam, oyster, and chicken tissues. The purpose of the method would be to extract and cleanup the compounds of interest (14-44 PFAS compounds, method dependent) from the matrix in such a way to concentrate them to increase sensitivity to the parts-per-trillion (ppt) range, and eliminate interferences from the matrix that can cause false positives and false negatives. This can happen due to signal enhancement or suppression. This is common with many other analytes, such as veterinary drugs, mycotoxins, pesticides, etc. It is crucial to eliminate as much interference as possible and can be accomplished through rigorous extraction and cleanup procedures, and the use of isotopically labeled internal standards.

Every method found has similarities, from the cleanup step to the instrument used. One of the methods has been adapted and validated by EPA for the determination of PFAS compounds in a pesticide formulation (see Table 1). Other methods may be capable of analyzing for PFAS in pesticide formulations but will require extensive validation in order to be used on a routine basis

for monitoring and enforcement. The initial work will require the examination of the confidential statement of formula to group pesticide types into categories to validate according to the similarity of the inerts. Once grouped, samples of each category can be analyzed using the proposed method in order to determine the precision and accuracy of the method. Once the methods are validated it may be possible to combine into a single but complex method.

In an email dated, 02/22/2023, from Gill Sonom, States Liaison, Office of Intergovernmental Relations, of the EPA about the use of EPA method 537.1, and 1633 for the analysis of PFAS compounds in pesticide formulations, to Senator Hettleman, the use of either method by sample dilution is discouraged. The only part that could be adopted is the instrumental analysis in both methods.

Comparison of PFAS Methods

In comparing the methods that are considered “official”, each was reviewed, and summarized in Table 1 found at the end of this document. The table rows list the method, version, year first published, sample matrix, number of compounds determined, preservative, holding temperature, hold time, sample preparation, type of calibration, analyte quantitation, any modifications allowed, and any modifications not allowed. There are five methods from the EPA (United States Environmental Protection Agency), three from ASTM (American Society for Testing and Materials International), and two from ISO (International Standards Organization). The two methods developed by the Analytical Chemistry Branch of the Office of Pesticide Programs, and the EPA will be discussed in the next section. There are six methods that can be used for drinking water, four methods that can be used for non-drinking water sources, five methods for solid waste, six methods for wastewater, two methods for soil, and one method for biosolids, sediment, and tissues (fish, shellfish, chicken). The United States Department of Agriculture (USDA) and the Centers for Disease Control (CDC) have methods for animal body fluids, and human body fluids which will not be discussed in this study.

The sample matrices that can be analyzed by these methods are drinking water, non-drinking water, solid waste, wastewater, ground water, soil, sediment, biosolids, and animal tissues. These matrices range from simple (water, soil, sediment) to more complex (animal tissue, and biosolids). The methods have been validated for fourteen to forty-four PFAS compounds. Five of the methods require some preservative for aqueous matrices. The holding temperature for all methods and matrices is 4 °C, and for one method -20 °C can also be used with a substantial extension of holding time. The holding time for the sample before injection is between fourteen and twenty-eight days for samples held at 4 °C, and 90 days for frozen samples. The holding time after extraction for analysis is fourteen to thirty days. Six of the methods use SPE (Solid Phase Extraction), the other four use no SPE cleanup step. For the solid methods, there is an initial extraction step followed by cleanup steps. All methods use LC-MS/MS (Liquid Chromatography-Mass Spectrometry/Mass Spectrometry) for the separation and determination of the compounds.

Calibration and quantitation are handled by external and internal standard methods. External standard methods do not use isotopic standards. Internal standards use isotopically labeled surrogate standards for recovery and quantitation purposes. This is commonly known as isotope dilution. Two ASTM methods do not allow any modifications to the method. Two methods are completely performance based. This means that the method can be modified and/or be used for any matrix as long as it is validated by the laboratory to show that the original quality control metrics are achieved. Modifications for methods usually are evaporation technique, separation technique, LC column, mobile phase composition, LC conditions, and some of the MS/MS conditions. Many of the modifications that may be needed are instrument specific, depending on the instrument manufacturer. This is especially true of the MS/MS conditions, as these vary by manufacturer. The three methods with no modifications allowed are all drinking water methods, and are sample collection and preservation, sample extraction, and QC requirements for the analysis.

Status Update on Federal Efforts to Certify a Method

Currently, the ACB (Analytical Chemistry Branch), ACL (Analytical Chemistry Laboratory), BEAD (Biological and Economic Analysis Division), OPP (Office of Pesticide Programs), OCSPP (Office of Chemical Safety and Pollution Prevention) of the EPA have developed and internally validated two methods for certain types of pesticide formulations and for fluoridated containers that are used in many mosquito control products, as well as analyzed samples provided by Maryland Department of Agriculture and Dr. Steven Lasee from Texas Tech University. In December 2021, the Massachusetts Department of Environmental Protection and PEER (Public Employees for Environmental Responsibility), published results of PFAS analysis of several mosquito control products used in the state of Massachusetts to control mosquito populations. This analysis found the total PFAS concentration in the range of non-detects – 2,500 ppb. The methods used were based upon LC-MS/MS technologies, and one of the methods used was not internally validated.

The ACB analyzed samples taken from mosquito control products used on the Eastern Shore by the Department's Mosquito Control Program, Permenone 30-30 and PermeSease 30-30. Three samples were also analyzed from the manufacturer of Permenone 30-30. The samples obtained from the manufacturer were a retained sample from a lot produced 9 days after the lot was purchased by Mosquito Control, and three samples were taken from different points along a recent Permenone 30-30 production line and from storage. Twenty-eight PFAS compounds were analyzed by the oily matrix method using LC-MS/MS and LC-HRAMS (Liquid Chromatography High-Resolution Accurate Mass Spectrometry) as a confirmation analysis. The oily matrix method is described in further detail below. The ACB found none of the targeted analytes in the samples from the Department nor in any product received from the manufacturer.

The ACL of the US EPA published a report dated March 04, 2021, on rinsing studies on selected fluoridated and non-fluoridated HDPE (High-Density Polyethylene) containers and a limited number of mosquito control products. There were seven fluoridated jugs/drums and two

non-fluoridated jugs. The method for the rinsates was developed to determine the PFAS concentration that could be rinsed from the inside and the outside of the containers. The method is straightforward and easy to perform. The unused non-fluoridated jugs (exterior = 0.79 ng total PFAS, interior = 0.17 ng total PFAS) have substantially less total PFAS than the unused fluoridated jugs and drums (21 – 345 ng total PFAS). The used 2.5-gallon jug had 15.2 ng total PFAS rinsed from the outside, and 8.6 ng total PFAS rinsed from the inside. The fluoridated drums have the highest PFAS content. This would indicate that the PFAS in pesticide formulations is actually being leached from the container. The USEPA has contacted pesticide manufacturers of mosquito control products, and they have switched from fluoridated containers to stainless steel containers or non-fluoridated containers.

An oily matrix method report was published by the EPA on September 28, 2021, for the validation of twenty-eight PFAS compounds. The method was validated using a clean oily matrix formulation containing no active ingredient. The oily matrix analyzed can include oil, petroleum distillates, or mineral oils that are used in pesticide formulations. The method limit of detection is 0.025 µg/kg (ppb or 25 ppt) for most of the analytes. Briefly, the method takes the oily sample and passes it through a silica-based Florisil SPE cartridge that is validated for pesticide analysis (for example, see EPA Method 3620C published in 2014). After loading the SPE cartridge, the matrix is washed off the cartridge with a mixture of solvents, leaving the PFAS compounds behind on the cartridge. The PFAS compounds are eluted off the SPE cartridge by another mixture of solvents, concentrated down to a known volume, and analyzed by LC-MS/MS using the instrument parameters described in EPA Method 537.1. Isotopically labeled surrogates were added prior to sample processing to assess signal enhancement and suppression, as well as recovery. There are interferences that can be expected that will lead to false positive identification and elevate quantitation levels. Recoveries varied throughout the study and do not appear to be concentration dependent.

On May 18, 2023, the EPA published a memorandum for ACB Project B23-05b, which involved the analysis of 10 pesticide products that were analyzed using a dilute and shoot method reported in “Targeted Analysis and Total Oxidizable Precursor Assay of Several Insecticides for PFAS” by Lasee, et.al., in *Journal of Hazardous Materials Letters*, 2022, 3, 100067. This article reported PFAS concentrations in the 10 products ranging from non-detects to 19.2 mg/kg (ppm) PFOS in the products. The samples were analyzed by two methods: 1) the method developed by the study author, and 2) the surfactant and oil method. Twenty-six PFAS analytes were screened in the EPA study and the Lasee method. There were three compounds added to the EPA study that were not included in the Lasee study.

The main difference between the two methods is the sample preparation step. Lasee’s method is a simple dilution method with a solvent/water mixture and using a single instrument for analysis. The ACB’s method involves a more intense extraction and clean up procedure to isolate the PFAS compounds from the sample matrix before instrumental analysis, reducing matrix interferences that give more accurate results and detection limits. Both methods use isotopically labeled standards and surrogates to monitor the performance of the method and to accurately

quantitate the compounds of interest. The ACB method used two different instruments to analyze the compounds: LC-MS/MS and LC/HRAMS (Liquid Chromatography-High Resolution Accurate Mass Spectrometry). The HRAMS instrument has higher selectivity than the MS/MS instrument. The results of the study showed no PFAS compounds, including PFOS, were detected above the method detection limits by either instrument.

Status Update on State and Federal Efforts to Regulate or Ban the Use of Pesticides Containing PFAs (5)

Most pesticide products contain substances in addition to the active ingredient(s) that are referred to as inert ingredients or sometimes as “other ingredients.” An inert ingredient generally is any substance (or group of similar substances) other than an active ingredient that is intentionally included in a pesticide product. Examples of inert ingredients include emulsifiers, solvents, carriers, aerosol propellants, fragrances, and dyes.

The EPA published “Pesticides; Proposed Removal of PFAS Chemicals from Approved Inert Ingredient List for Pesticide Products” (EPA-HQ-OPP-2022-0542; FRL-9985-01-OCSPP) in the Federal Register Volume 87, No. 176, pp. 56051-56053. EPA proposed to remove twelve chemicals from the current list of inert ingredients approved for use in pesticide products because these have been identified as PFAS compounds, and they are no longer used in any pesticide products. The table below lists the 12 PFAS compounds that have been removed from the approved list of inerts.

Compound	CAS Reg. No.
2-Chloro-1,1,1,2-tetrafluoroethane	2837-89-0
α -(Cyclohexylmethyl)- ω -hydropoly(difluoromethylene)	65530-85-0
Dichlorotetrafluoroethane	1320-37-2
1,1,1,2,2-pentafluoroethane	354-33-6
Hexafluoropropene, polymer with tetrafluoroethylene	25067-11-2
Montmorillonite-type clay treated with polytetrafluoroethylene	No CAS Reg. No.
α -Chloro- ω -(1-chloro-1-fluoroethyl)-poly(difluoromethylene)	131324-06-6
α -Chloro- ω -(2,2-dichloro-1,1,2-trifluoroethyl)-poly(difluoromethylene)	79070-11-4
α -(2,2-dichloro-2-fluoroethyl)- ω -hydro-poly(difluoromethylene)	163440-89-9
α -Fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-poly(difluoromethylene)	65530-66-7
α -Hydro- ω -hydroxy-poly(oxy-1,2-ethanediyl) ether with α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene) (1:1)	65545-80-4
1,1,1,2,3,3,3-Heptafluoropropane	431-89-0

None of the above are currently being used as inert ingredients in any pesticide products. The EPA will continue to evaluate any new inert ingredients submitted for use in pesticide product manufacturing.

The EPA issued a letter on March 16, 2022 to the manufacturers, processors, distributors, users, and those involved with the disposal of fluorinated polyolefin containers. This was issued after the ACB's study of fluorinated and non-fluorinated containers. The agency issued the letter to remind the industry of the PFAS issue to help prevent unintended PFAS formation and contamination, and to emphasize the requirement under the Toxic Substances Control Act (TSCA) as it related to PFAS and fluorinated polyolefins. This effort is in line with the PFAS Strategic Roadmap. The process of fluorinating polyolefins involves the modification of certain types of polymers (plastics), using fluorine to create a high-performance barrier that is meant to mitigate permeation through container walls, as well as protect against environmental weathering and degradation of the plastic. Fluorination can occur before or after the shaping process of the HDPE containers or similar plastic and the fluorinated containers can be used to store and transport a variety of products.

To date, the agency has published groundwater cleanup guidance; issued a proposal ensuring that new uses of certain chemicals within the class cannot be manufactured or imported without notification and review under the Toxic Substances Control Act; released drinking water health advisories for several PFAS chemicals under the Safe Drinking Water Act; and announced a new testing method for 11 additional PFAS chemicals in drinking water. All ongoing EPA actions can be found here. The agency also announced about \$4.8 million for new research focused on managing PFAS in the agriculture sector and highlighted new ways that existing programs, like state revolving funds (SRFs), can be used to address the chemicals.

The EPA also announced its intent to propose a new rule designating PFOA and PFOS as hazardous substances under the Superfund law. The action is in line with the agency's PFAS Strategic Roadmap. By designating the chemicals under the Comprehensive Environmental Response, Compensation and Liability Act, as the Superfund law is formally known, the federal government may take actions at a contaminated site or transfer necessary funds and management responsibility to a state or tribe. A Superfund designation would require facilities to report on PFOA and PFOS releases that meet or exceed selected reportable quantities and would enhance the ability of federal, tribal, state and local authorities to obtain information regarding the location and extent of those releases. The designation would also allow the EPA or other agencies to recover cleanup costs from the responsible party or require said party to conduct the cleanup.

The Maryland Department of Agriculture will closely monitor the EPA's efforts to further regulate and eliminate PFAS in pesticide products. EPA has taken steps to ensure that inerts, and containers are tightly regulated at the federal level. The Department will begin to review the Confidential Statement of Formula (CSF) for all 13,575 pesticide products that are registered in the state of Maryland, for 2023, to determine if there are any PFAS compounds in the pesticides. The level of PFAS compounds when used as an inert ingredient can be anywhere from 100 mg/kg to 1,000 mg/kg. To date, 750 CSFs have been reviewed and found to not contain any PFAS compounds as an inert ingredient. If PFAS compounds are found as inerts, the Department

will work with the EPA to make a determination on whether to revoke the registration of these products. The decision to revoke a registration cannot be taken lightly and must be based upon the best available science. It is essential to have standards developed so that proper comparisons be made in order to base a valid conclusion on whether the level of PFAS found is a detrimental factor to the environment, animal health, or human health.

The CSF's will also be reviewed and grouped according to the inert ingredients that they contain. This grouping is necessary in order to develop and validate methods for the determination of trace amounts of PFAS compounds in the formulations themselves. The methods developed will help regulatory agencies determine if there are any PFAS compounds in any pesticide products. This method development will be lengthy due to the types of products, and their forms, that are registered.

Conclusions and Recommendations

After reviewing available literature and governmental data, there is a lack of information concerning the contribution of PFAS in pesticide formulations to the impact of PFAS in the environment and exposure to humans. In order to better understand the impact of PFAS in pesticide formulations, laboratory analysis of PFAS in formulations must be at the forefront of any environmental or human impact studies or decision-making policy. Without reliable data about formulation contamination, there can be no reliable environmental or toxicological analysis. Therefore, we are unable to make any policy determination at this juncture.

The range of pesticide formulation types that are registered in the state of Maryland makes the analysis for PFAS very challenging. Since pesticide formulations contain a variety of inert ingredients, this further complicates the development and validation of a one-size-fits-all method. The inert ingredient diversity can introduce potential interferents in the analysis if proper sample preparation and cleanup is not performed prior to instrumental analysis. Another aspect of this is the type of instrument used. The use of an LC-HRAMS (Liquid Chromatography High-Resolution Accurate Mass Spectrometer) will eliminate many of these false positive results. The use of the proper method is crucial to the evaluation of the impact of PFAS in pesticide formulations on the environment and human health.

There are two recommendations from the workgroup. The first is to follow EPA's lead on the formulation. The EPA is currently developing a method specifically to test various pesticide formulations. The second is to analyze formulations that are registered with the Maryland Department of Agriculture's State Chemist Section in order to acquire baseline data. Following EPA's lead would fit into the agency's PFAS Roadmap but would take time. The second recommendation may be the most expedient.

The analysis of pesticide formulations would provide the data needed to make well-informed decisions based upon good science. This route would necessitate the establishment of a PFAS testing program within the State Chemist Section. The section has over 30 years of experience dealing with pesticide formulations, whether analyzing for the active ingredients or contaminants in the formulations itself. The section has over 30 years of experience in the analysis of

contaminants in environmental samples; including water, groundwater, sediment, soil, vegetation, and animal tissue. The analysis of formulations would require initial funding for a room renovation and equipment purchasing.

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Comparison	Method Author											
	US EPA ORD	US EPA ORD	US EPA ACB	US EPA ACB	USEPA Office of Water	USEPA Office of Solid Waste	USEPA Office of Water	ASTM	ASTM	ASTM	ISO	ISO
Method	537	537.1	PFAS in Oily Matrix (using modified 537.1)	Method for analysis of PFAS in Pesticide Products Containing Non-ionic Surfactants and Non-volatile Oils (modified 8327)	533	8327	1633	D8421	D7968	D7979	25101	51675
Version	1.1	1.0	ACB Project B21-02	ACB Project B23-05b	EPA Document No. 815-B-19-020, version not assigned	0 (2021)	0 (Draft)	2021	2017	2020	2009	2019
Year first published	2009	2018	2021	2023	2019	2019	2021	2021	2014	2015	2009	2019
Sample matrix ^a	DW	DW	Pesticide products formulated in oil, petroleum distillates, mineral oils	Pesticide products formulated in non-ionic surfactants and oil	DW	Non-DW, DW, SW, WW	Non-DW, GW, SW, WW, leachates; Solid: Soil, Sediment, Biosolids, Tissue (fish, shellfish)	Non-DW, GW, SW, WW	Soil/Solids	Non-DW, GW, SW, WW	DW, GW, SW, WW	DW, SW, WW
Compounds Determined	14	18	28	29	25	24	40	44	31	31	2 (focus on linear isomers)	30 (focus on linear isomers)
Preservative	Tris Buffer	Tris Buffer	None	None	Ammonium Acetate	None	None	None	None	None	Dechlorinating	Dechlorinating

											Agent	Agent
Temperature	4° C	4° C	Not specified	Not specified	4° C	4° C	@ 0-6° C or @ <-20° C	4° C	4° C	4° C	4° C	4° C
Hold time (Extract/Analysis)	14/28 days	14/28 days	Not specified	Not specified	28/28 days	14/30 days	Samples - 90 days @ -20° C or 7 days @ 0-6° C Extracts- 28 days @ 0-4° C or 90 days (if not testing for ether sulfonates or NFDHA)	28 days	28 days	28 days	14 days	28 days
Sample Preparation	SPE Cartridge (SDVB)	SPE Cartridge (SDVB)	SPE Cartridge (Florisil)	QuEChERS liquid extraction followed by SPE Cartridge (Florisil)	SPE Cartridge with a positively charged amino ligand (WAX=weak anion exchange)	Entire sample processed in original container, direct aqueous injection	SPE Cartridge (WAX)	Entire sample processed in original container, spiked with surrogates add MeOH, mix, filter, adjust pH	Spike with surrogates, tumble with MeOH:H2O, centrifuge, extract, filter, adjust pH	Entire sample processed in original container, spiked with surrogates add MeOH, mix, filter, adjust pH	SPE	SPE, weak anion exchange
Instrument	LC-MS/MS	LC-MS/MS	LC-MS/MS LC-HRAM (for confirmation)	LC-MS/MS LC-HRAM (for confirmation)	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS
Calibration	External standards (14) with isotopically labeled internal standards (3)	External standards (18) with isotopically labeled internal standard (3)	External standards (28) with isotopically labeled internal standards (3)	isotope dilution standards and isotopically labeled internal standards	isotope dilution standards (16) and isotopically labeled internal standards (3)	External Standards	Isotope dilution standards (24) and isotopically labeled internal standards (7)	External standards (24) (isotope dilution optional)	External Standards	External standards (24) (isotope dilution optional)	Internal standards (2)	Internal (18) or external standards
Analyte Quantitation	Internal Standard (non-	Internal Standard (non-	Internal standard (non-	Internal standard	Internal standard	External standards	Internal Standard	External standard	External standard	External standard	Internal standard	Internal standard

	isotope dilution)	isotope dilution)	isotope dilution)	(isotope dilution)	(isotope dilution)	(non-isotope dilution)	(isotope dilution)	(isotope dilution optional)	(non-isotope dilution)	(isotope dilution optional)	(isotope dilution)	(isotope dilution) or external standard)
Modification Allowed	Evaporation technique, separation technique, LC column, mobile-phase composition, LC conditions, MS and MS/MS conditions	Evaporation technique, separation technique, LC column, mobile-phase composition, LC conditions, MS and MS/MS conditions	N/A	N/A	LC columns, LC conditions, sample volume (maintain SPE ratio)	Performance based method	Performance based method	Limited Performance based method	Limited Performance based method	Limited Performance based method	N/A	N/A
Modification Not Allowed	Sample collection and preservation, sample extraction and QC Requirements	Sample collection and preservation, sample extraction and QC Requirements			Preservation, QC requirements, extraction procedures							

^a Matrices: DW = Drinking Water, Non-DW = non-Drinking Water, SW = Solid Waste, WW = Waste Water, GW = Ground Water