

Forever Pesticides: A Growing Source of PFAS Contamination in the Environment

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BACKGROUND: Environmental contamination by fluorinated chemicals, in particular chemicals from the per- and polyfluoroalkyl substances (PFAS) class, has raised concerns around the globe because of documented adverse impacts on human health, wildlife, and ecosystem quality. Recent studies have indicated that pesticide products may contain a variety of chemicals that meet the PFAS definition, including the active pesticide ingredients themselves. Given that pesticides are some of the most widely distributed pollutants across the world, the legacy impacts of PFAS addition into pesticide products could be widespread and have wide-ranging implications on agriculture and food and water contamination, as well as the presence of PFAS in rural environments.

OBJECTIVES: The purpose of this commentary is to explore different ways that PFAS can be introduced into pesticide products, the extent of PFAS contamination of pesticide products, and the implications this could have for human and environmental health.

METHODS: We submitted multiple public records requests to state and federal agencies in the United States and Canada and extracted relevant data from those records. We also compiled data from publicly accessible databases for our analyses.

DISCUSSION: We found that the biggest contributor to PFAS in pesticide products was active ingredients and their degradates. Nearly a quarter of all US conventional pesticide active ingredients were organofluorines and 14% were PFAS, and for active ingredients approved in the last 10 y, this had increased to 61% organofluorines and 30% PFAS. Another major contributing source was through PFAS leaching from fluorinated containers into pesticide products. Fluorination of adjuvant products and “inert” ingredients appeared to be limited, although this represents a major knowledge gap. We explored aspects of immunotoxicity, persistence, water contamination, and total fluorine load in the environment and conclude that the recent trend of using fluorinated active ingredients in pesticides may be having effects on chemical toxicity and persistence that are not given adequate oversight in the United States. We recommend a more stringent risk assessment approach for fluorinated pesticides, transparent disclosure of “inert” ingredients on pesticide labels, a complete phase-out of post-mold fluorination of plastic containers, and greater monitoring in the United States. <https://doi.org/10.1289/EHP13954>

Introduction

Pesticides are commonly used in the United States and around the world to kill or suppress certain organisms on farmland and in areas where people live and work. Although pesticides are often efficacious at killing or preventing the growth of target

organisms, they are widely regarded as causing serious unintended harms to both humans and nontarget biota. In the United States alone, roughly 450 million kg of pesticide active ingredients were applied in an estimated 5.3 million cumulative km²-treatments of farmland throughout the country in 2021.¹

Therefore, the enormous potential for human exposure and environmental contamination belies the importance of understanding complete product compositions and their environmental fate and transport. Pesticide products generally contain two types of ingredients: active and “inert.” Active ingredients are the primary components in pesticide products that kill or suppress the targeted organism.² “Inerts” are every other ingredient added to the pesticide product, including emulsifiers, solvents, carriers, aerosol propellants, fragrances, and dyes.³ However, far from being inert, many of these ingredients have chemical properties that can influence the toxicity or alter the bioavailability of the active ingredient or have unintended off-target effects themselves to people and wildlife.^{4,5} Unlike active ingredients, “inerts” are not required to be publicly disclosed on the pesticide label⁶ and toxicity testing is limited.⁵ This lack of transparency and insufficient toxicity testing—in the pesticide context and many others—accomplishes two things from a public health perspective: It can *a*) hamper the ability of medical professionals to effectively treat patients who fall ill following pesticide exposure and *b*) shield companies from accountability regarding the harms from their products.^{5,7,8}

In agriculture, pesticide products are commonly applied with adjuvants, which are separate products that can reduce drift/volatilization, facilitate application, or enhance pesticidal effects of pesticide products.⁹ Adjuvant ingredients are widely used in US agriculture, as demonstrated by an analysis of usage data in the state of California.⁹

Fluorination is used to modify chemical attributes, such as stability and lipophilicity, improve stereochemical specificity, and increase residual activity of pesticide ingredients.¹⁰ Pesticide active ingredients are commonly fluorinated, with insecticides and

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N.D.’s employer, the Center for Biological Diversity, currently has active litigation against the US EPA involving some active ingredients that happen to be PFAS for failure to consult under the Endangered Species Act and failure to comply with the Federal Insecticide, Fungicide, and Rodenticide Act. The PFAS classification and extent of fluorination of the active ingredients are not at issue in the litigation. N.D. has provided scientific support for these lawsuits. K.B.’s employer, Public Employees for Environmental Responsibility (PEER), currently has active litigation against Inhance Technologies, LLC, involving formation of PFAS during the fluorination of plastic containers contrary to EPA regulations. K.B. is a Declarant in the lawsuit and has provided scientific support for this lawsuit. K.B., on behalf of PEER, has publicly taken the position that post-mold fluorination of plastic containers is dangerous to human health and the environment and should be discontinued. K.B. and PEER are also representing current and former government scientists on issues relating to PFAS, and PFAS in pesticides. K.B. and PEER have also been involved with Freedom of Information Act (FOIA) litigation against EPA for PFAS related issues. All other authors declare they have nothing to disclose.

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acaricides more likely to be highly fluorinated.¹¹ Fluorination can contribute to the molecular stability of active ingredients—both *in vivo* and in the broader environment—and can influence lipophilicity, which can alter membrane permeability and binding to target proteins.¹⁰ The most common chemotype for fluorinated active ingredients is a trifluoromethyl (−CF₃) group followed by a monofluoromethyl group (−CFH₂).¹¹

Numerous patents have demonstrated ways in which fluorinated “inerts” can expedite dispersal of the sprayed pesticide on targeted surfaces such as leaves, aid in surfactancy, and facilitate the penetration of the pesticide into living organisms.¹² The fluorination of inert ingredients can help prevent the formation of foam in the pesticide formulation to ensure efficient spreading of the pesticide after spraying,^{12,13} and fluorinated inerts are also used as propellants in aerosol pesticide products.¹⁴ Given that many adjuvant and inert ingredients perform similar functions, it is assumed that at least some adjuvant ingredients are fluorinated.¹⁵

One subset of fluorinated molecules is per- and polyfluoroalkyl substances (PFAS). PFAS are a serious environmental health concern owing to their highly persistent nature,¹⁶ often potent toxicities,¹⁷ potential to bioaccumulate,¹⁸ and widespread presence in people, animals, and the broader environment.^{19,20} Through its PFAS Strategic Roadmap, the US Environmental Protection Agency (EPA) in 2021 committed to not only facilitate the remediation of legacy PFAS contamination but also to intervene to limit the introduction of unnecessary new PFAS into the environment.²¹

A widely used definition of PFAS comes from the Organisation for Economic Cooperation and Development (OECD) and encompasses almost any chemical with at least one perfluorinated methyl group (−CF₃) or a perfluorinated methylene group (−CF₂−).^{22,23} Given the broad nature of this definition, PFAS are often subcategorized by the length of their carbon chain. For the purposes of this commentary, we have further classified PFAS as long-chain, short-chain, or ultrashort-chain, which respectively contain ≥6, 4–5, and ≤3 fully fluorinated carbon atoms. Although all PFAS are considered extremely persistent owing to the strength of the carbon–fluorine bond, some may differ significantly in other chemical properties, such as mobility, lipophilicity, and potential to bioaccumulate.²⁴

Given the diverse array of health impacts that have been linked to PFAS exposure,²⁵ it is important to understand the extent to which the inclusion of carbon–fluorine bonds within pesticide ingredients is impacting persistence and toxicity. When proposing drinking water limits for six PFAS, the US EPA found that reduced exposure would result in a lower prevalence of kidney cancers, heart attacks, strokes, and developmental effects, as well as a general reduction in harms to the immune, developmental, cardiovascular, hepatic, endocrine, metabolic, reproductive, and musculoskeletal systems of US residents.²⁶ The majority of studies on PFAS toxicity have focused on just a few compounds, but efforts to catalog the toxicity of other PFAS have indicated shared toxicity end points.^{27,28}

The purpose of this commentary is to explore ways that PFAS can be introduced into pesticide products, the extent of PFAS contamination, and the implications this could have for human and environmental health. Here we have identified multiple pathways by which PFAS are introduced into pesticide products—both intentionally and unintentionally—and the regulatory shortcomings that prevent a faithful accounting of the risks posed by this class of chemicals. By focusing on pathways of PFAS introduction, our goal with this commentary is to ultimately identify ways that regulators could reduce PFAS in these products and more fully account for their human and environmental health harms in the pesticide registration process.

Methods

Information Sources Used in This Commentary

Information on the number of currently registered active ingredients, fluorinated inert ingredients, and fluorinated adjuvant ingredients were obtained from public records requests to various state-level government agencies in the United States, US federal agencies, and Canadian agencies and are cited in text in the “Methods” or “Discussion” sections. Multiple publicly accessible databases were also searched for relevant adjuvant ingredient information and water detections of fluorinated active ingredients and are also cited in text in the “Methods” and “Discussion” sections. Data sources used in this commentary can be found in Table 1.

Additional Analyses Conducted for Active Ingredients

As of 31 December 2021, the US EPA had 1,157 pesticidal active ingredients registered with the agency (Excel Table S1).²⁹ Active ingredients fell into three different categories: biopesticide, antimicrobial, and conventional. Biopesticides⁴⁸ are naturally occurring chemicals or living organisms—often used in organic agriculture—that do not contain carbon–fluorine bonds. Antimicrobials⁴⁹ are often used indoors in relatively lower amounts. Conventional active ingredients⁵⁰ are often thought of as “typical” pesticides—mainly synthetic chemicals used widely in agriculture, around people’s homes and in green spaces to kill unwanted insects, plants, rodents, or fungi. These ingredients have a higher potential for broader environmental contamination because they are often used outdoors and in higher quantities than biopesticides or antimicrobials.^{51,52} Therefore, we curated the list of active ingredients we received in our public records request down to 471 unique, conventional active ingredients to determine how many were organofluorines or PFAS (Excel Tables S1–S3).

In curating our list of 1,157 pesticidal active ingredients down to 471 unique, conventional active ingredients, we

- Mined US EPA’s Pesticide Product and Label System (PPLS) database,⁵³ the Pesticide Chemical Search tool,⁵⁴ and other online materials to identify and exclude any active ingredient

Table 1. Public records, communications, and database sources used in this commentary.

Section	Sources
Active ingredients	US EPA FOIA response ²⁹
Inert ingredients	US EPA FOIA responses, ^{30,31} US EPA InertFinder Database, ³² Health Canada PMRA List of Formulants, ³³ email communication with Health Canada’s Senior Scientific Screening Officer (N. Donley, personal communication)
Adjuvant ingredients	TELUS Label Search, ³⁴ California Department of Pesticide Regulation Public Records Act Request, ³⁵ Washington State Department of Agriculture Spray Adjuvant Ingredients List ³⁶
Storage container leaching	Analytical testing reports from Eurofins Lancaster Laboratories Env, LLC. ^{37–42} and Alpha Analytical, ⁴³ US EPA. Analysis of PFAS in selected mosquito control products from the Maryland Department of Agriculture, ⁴⁴ US EPA. Verification Analysis for PFAS in Pesticide Products. ⁴⁵
Water contamination	USGS. Dissolved Pesticides in Weekly Water Samples from the NAWQA Regional Stream Quality Assessments (2013–2017). ⁴⁶
Pesticide usage	USGS. Preliminary estimated annual agricultural pesticide use for counties of the conterminous United States. ⁴⁷

Note: EPA, Environmental Protection Agency; FOIA, Freedom of Information Act; NAWQA, National Water-Quality Assessment; PFAS, per- and polyfluoroalkyl substances; PMRA, Canada’s Pest Management Regulatory Agency; USGS, US Geological Survey.

that met the definition of an antimicrobial or biopesticide. Antimicrobial pesticides are substances or mixtures of substances used to destroy or suppress the growth of harmful microorganisms, such as bacteria, viruses, or fungi, on inanimate objects and surfaces. Biopesticides are any plant incorporated protectant (PIP), live organism, or naturally occurring extracts from live organisms (e.g., peptides, alcohols, oils, pheromones, extracts). We also excluded any active ingredient whose sole purpose was not for pesticidal use, such as nitrogen stabilization.

- Identified and excluded different precursor forms of the same pesticide because the active pesticide molecule was identical (e.g., dicamba was only represented once in our list even though it had many different registered salt forms). We also identified and excluded different purified isomers or enantiomers that were present in mixtures of a previously registered active ingredient (e.g., alpha-cypermethrin and zeta-cypermethrin were excluded from our list because they were simply two isomers that were present in the previously registered cypermethrin). We also identified and excluded active ingredients that were structurally identical but in a different phase from an active ingredient on our list (e.g., amorphous silica and silicon dioxide were reduced down to a single entry on our list).
- Identified and removed products that only had “technical” or “manufacturing use only” products registered, because we were interested only in active ingredients used in end-use products.

US Geological Survey Water Data Analysis

Between 2013 and 2017, the US Geological Survey (USGS) analyzed 482 wadable streams for pesticide contaminants in five regions of the United States (Northwest, California, Midwest, Southeast, and Northeast). The methodology used is described in five regional reports,^{55–59} and data are available for downloading from the USGS website.⁴⁶ We manually identified all analyzed active ingredients that met the OECD PFAS definition, as well as degradates (metabolites) of those active ingredients, in the site’s Table 3 text file and extracted the available detection and water concentration data on those chemicals from Data Tables 4–8 on the same site.⁴⁶ Data extracted and compiled included the number of positive detections and maximum detected concentrations for 29 analytes (13 PFAS active ingredients plus 16 fluorinated degradates).

Discussion

How PFAS Are Introduced into Pesticides

We sought to document and understand ways in which PFAS were introduced into pesticides and the extent of PFAS contamination in pesticide products. The following sections detail our analyses. There are multiple ways that PFAS can be introduced into pesticide products, which can facilitate their deposition into the environment. We have broadly categorized these PFAS contamination pathways as intentional and unintentional. Below are examples of each.

Intentional addition of PFAS. Active ingredients. Of the 471 unique, conventional active ingredients that were currently registered in the United States, 107 (23%) contained at least one carbon–fluorine bond and 66 (14%) met the OECD definition²² of PFAS (Figure 1 and Table 2; Excel Tables S3–S5) (see the “Methods” section for details). Of the 54 conventional active ingredients that had been approved in the most recent 10 y, the proportion of fluorination increased dramatically with 33 (61%) classified as organofluorines and 16 (30%) as PFAS (Figure 1 and Table 2; Excel Tables S3–S5).

The trend of increasing fluorination of active ingredients in the United States in recent years was consistent with trends in other countries¹⁰ and with the ability of fluorination to impart chemical properties on pesticides that were desirable to manufacturers and users, particularly the addition of a $-\text{CF}_3$ moiety.¹¹ In fact, most of the PFAS active ingredients contained a $-\text{CF}_3$ group as the sole criteria for their inclusion as PFAS in this commentary (Table 2 and Figure 2; Excel Tables S4 and S5).

Two active ingredients stood out as having a significantly higher degree of fluorination than the others: broflanilide and pyrifluquinazon (Figure 2; Excel Tables S4 and S5). Both contain a highly fluorinated side chain that is structurally similar to hexafluoropropylene oxide,⁶² a component of the highly toxic, known water contaminant GenX. However, despite both having a similar degree of fluorination, the parent molecules differ in their relative persistence as designated by the US EPA. Broflanilide is considered highly persistent, with the parent molecule having soil and aqueous half-lives in the range of 5–6 y.⁶³ The US EPA has found that the parent broflanilide and its fluorinated degradates have the potential to bioconcentrate and are likely to accumulate in the environment over time.⁶³ Despite these alarming chemical properties, the US EPA concluded that the pesticide met the registration standard under US pesticide

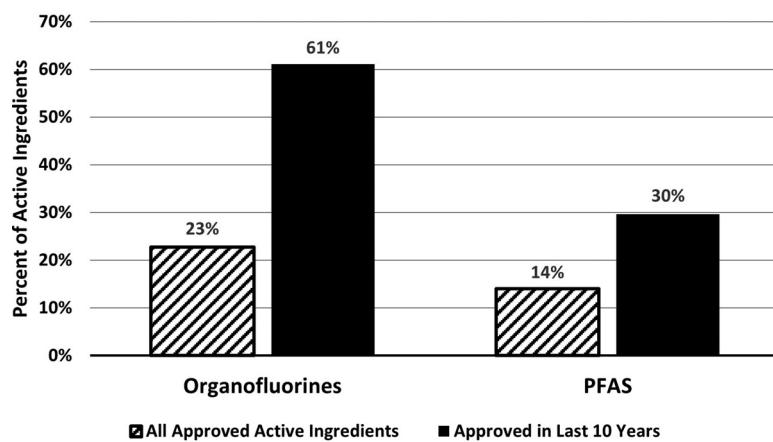


Figure 1. Percentage of conventional US pesticide active ingredients that were organofluorines or PFAS. The striped bars denote the percentage of all US-approved active ingredients ($n=471$) that were organofluorines (left) or PFAS (right) as of 2021. The solid bars denote the percentage of active ingredients approved between 2012 and 2021 ($n=54$) that were organofluorines (left) or PFAS (right). For all active ingredients, 107/471 (23%) were organofluorines and 66/471 (14%) were PFAS. For active ingredients approved between 2012 and 2021, 33/54 (61%) were organofluorines and 16/54 (30%) were PFAS. Note: PFAS, per- and polyfluoroalkyl substances.

law.⁶³ The parent molecule of pyrifluquinazon, on the other hand, is classified by the US EPA as nonpersistent, with soil and aqueous half-lives ranging from 1–16 d.⁶⁴ Extractable degradates were similarly short-lived; however, sediment-bound degradates were characterized as very persistent.⁶⁴ No studies on the terminal fluorinated

Table 2. PFAS active ingredients approved in the United States and associated registration dates.

CAS No.	Registration date	Active ingredient name ^a
50594-66-6; 62476-59-9	20 August 2018; 20 March 1987	Acifluorfen; sodium acifluorfen
1861-40-1	22 March 1972	Benfluralin
352010-68-5	24 April 2015	Bicycypyrone
82657-04-3	2 October 1985	Bifenthrin
1207727-04-5	14 January 2021	Broflanilide
63333-35-7	3 October 1985	Bromethalin
122453-73-0	19 January 2001	Chlorfenapyr
180409-60-3	27 June 2012	Cyflufenamid
400882-07-7	9 May 2014	Cyflumetofen
97886-45-8	18 June 1991	Dithiopyr
55283-68-6	2 May 1989	Ethalfluralin
120068-37-3	1 May 1996	Fipronil
104040-78-0	14 May 2007	Flazasulfuron
158062-67-0	26 September 2003	Flonicamid
79241-46-6	25 August 1986	Fluazifop-P butyl
79622-59-6	10 August 2001	Fluazinam
181274-17-9	29 September 2000	Flucarbazone-sodium
131341-86-1	5 October 1995	Fludioxonil
142459-58-3	8 April 1998	Flufenacet
62924-70-3	27 May 1983	Flumetralin
2164-17-2	28 May 1974	Fluometuron
239110-15-7	30 January 2008	Fluopicolide
658066-35-4	2 February 2012	Fluopyram
59756-60-4	31 March 1986	Fluridone
56425-91-3	4 December 1989	Flurprimidol
958647-10-4	13 March 2018	Flutianil
66332-96-5	12 March 1996	Flutolanil
69409-94-5	25 March 1983	Fluvalinate
72178-02-0; 108731-70-0	11 September 1987; 10 April 1987	Fomesafen; sodium salt of fomesafen
76703-62-3; 91465-08-6	31 March 2004; 13 May 1988	gamma-Cyhalothrin; lambda-cyhalothrin
86479-06-3	10 March 1994	Hexaflumuron
67485-29-4	30 September 1982	Hydramethylnon
173584-44-6	30 October 2000	Indoxacarb
141112-29-0	15 September 1998	Isoxaflutole
77501-63-4	1 April 1987	Lactofen
1417782-03-6	26 June 2019	Mefentrifluronazole
139968-49-3	3 August 2007	Metaflumizone
27314-13-2	19 March 1975	Norflurazon
116714-46-6	25 September 2001	Novaluron
121451-02-3	21 September 2001	Noviflumuron
1003318-67-9	31 August 2015	Oxathiapiprolin
42874-03-3	15 June 1981	Oxyfluorfen
219714-96-2	27 September 2004	Penoxsulam
183675-82-3	29 February 2012	Penthiopyrad
117428-22-5	30 November 2012	Picoxystrobin
29091-21-2	7 February 1992	Prodiamine
94125-34-5	3 May 1995	Prosulfuron
365400-11-9	9 August 2007	Pyrasulfotole
179101-81-6	24 April 2008	Pyridalyl
337458-27-2	3 January 2013	Pyrifluquinazon
447399-55-5	15 February 2012	Pyroxasulfone
422556-08-9	27 February 2008	Pyroxsulam
372137-35-4	3 September 2009	Saflufenacil
946578-00-3	6 May 2013	Sulfoxaflor
79538-32-2	17 January 1989	Tefluthrin
335104-84-2	29 November 2007	Tembotricone
112281-77-3	14 April 2005	Tetraconazole
1229654-66-3	10 March 2021	Tetraniliprole
88-30-2	21 August 1964	TFM

Table 2. (Continued.)

CAS No.	Registration date	Active ingredient name ^a
1220411-29-9	25 September 2020	Tiafenacil
122454-29-9	2 May 2007	Tralopyril
141517-21-7	20 September 1999	Trifloxystrobin
290332-10-4	29 September 2003	Trifloxysulfuron-sodium
68694-11-1	24 October 1991	Triflumizole
1582-09-8	4 December 1968	Trifluralin
126535-15-7	4 June 1996	Triflusulfuron-methyl

Note: CAS, Chemical Abstracts Service; EPA, Environmental Protection Agency; PFAS, per- and polyfluoroalkyl substances; TFM, 3-trifluoromethyl-4-nitrophenol.

^aData in the table were extracted from a public records request to the US EPA.²⁹ From this list, PFAS pesticides were manually identified and extracted for this table (see the “Methods” section for more detail).

degradates of pyrifluquinazon were analyzed by the US EPA, prompting US EPA scientists to convey that “we are concerned that the total accumulation of all PFAS degradates both known and unknown will be a risk issue.”⁶⁵

“Inert” ingredients. A public records request to the US EPA, which the agency responded to in December of 2022, indicated that the agency had 24 registered inert ingredients that it had identified as PFAS or that the agency suspected may be PFAS.³⁰ The provided list appeared to have been compiled of both PFAS inerts and fluorinated inerts that were not PFAS. Since the US EPA produced the list of 24, the agency canceled 12 that were not in any currently registered pesticide products⁶⁶ and we identified one as not having any carbon–fluorine bonds, leaving 11 currently registered organofluorine inert ingredients (Table 3). We confirmed this list of 11 by searching for “fluoro” in the ingredient name field on the US EPA’s Inert Finder database.³²

Of the 11 US EPA-registered organofluorine inert ingredients, 8 met the OECD definition of PFAS (Table 3 and Figure 2). Four of these 11 ingredients were approved for both food and nonfood use, whereas the rest were only for nonfood use.³² All the food-use organofluorine inerts had been exempted from a tolerance,^{67,68} meaning that any level of these ingredients was legal on food. Interestingly, 5 of these organofluorine inerts were not in any US-registered pesticide products, whereas 6 were present in 1–67 currently registered products (Table 3).³¹ Information on which specific products contained these ingredients was considered “confidential business information” by the US EPA, so it was unclear whether these products were widely used or how they were used.

Canada’s Pest Management Regulatory Agency (PMRA) has compiled a list of currently registered inerts (which it calls “formulants”) and updates that public list every 6 months.³³ As of 1 October 2022, there were eight organofluorine inert ingredients registered in the country, with seven being PFAS (Table 3). These eight organofluorine inerts were present in anywhere from 1 to 20 Canadian pesticide products (N. Donley, personal communication) (Table 3).

Notably, one inert ingredient approved in both the United States and Canada for both food and nonfood use was the incredibly persistent polytetrafluoroethylene (PTFE), known by the brand name Teflon (Table 3 and Figure 2). Although chemical manufacturers and their consultants consider fluoropolymers like PTFE to be less toxic than their nonpolymeric PFAS counterparts,⁶⁹ other researchers have identified serious concerns with their production and use.⁷⁰ For instance, PTFE can often be contaminated with nonpolymeric PFAS—at concentrations in the parts-per-million range, well above human toxicity thresholds.⁷⁰ This, coupled with its extreme persistence and the inability to recover PTFE once it has been dispersed, makes its use particularly problematic.

During peer review of this manuscript, the US EPA revised the number of products it believes contain PTFE from the 14 it

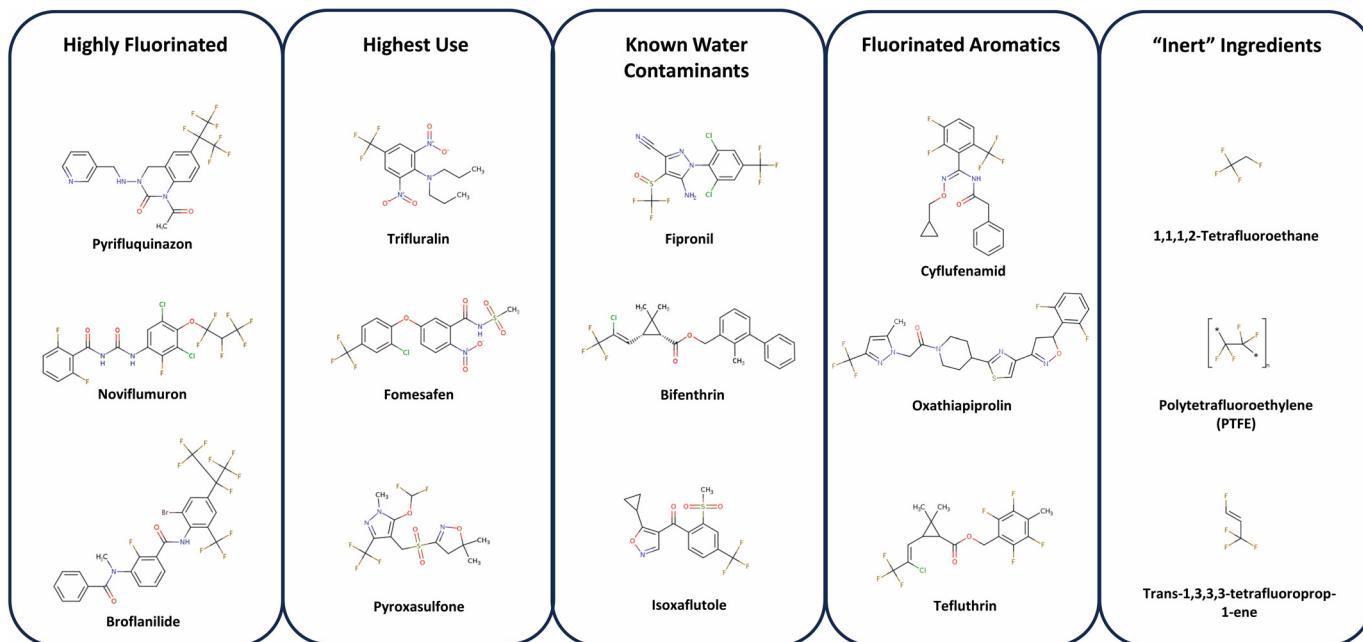


Figure 2. Examples of PFAS chemicals approved for use in US pesticide products. The “highly fluorinated” grouping is the approved PFAS active ingredients with the longest fluorinated chains. The “highest use” grouping is the approved PFAS active ingredients with the highest use by volume, as estimated by the US Geological Survey (Excel Table S6). The “known water contaminants” grouping is the approved PFAS active ingredients that have been widely reported in the literature and identified by government monitoring to be major water contaminants in the United States. The “fluorinated aromatics” grouping displays a few examples of the approved PFAS active ingredients that have fluorinated aromatic structures in addition to a $-CF_3$ moiety. The “inert” ingredients” grouping displays the US- and Canada-approved inert ingredients that are present in the most pesticide products (Table 3). Structure images were obtained from US EPA’s CompTox Chemicals Dashboard.^{60,61} Note: EPA, Environmental Protection Agency; PFAS, per- and polyfluoroalkyl substances.

told us in our earlier public records request (Table 3) to zero and proposed to remove PTFE from its list of approved inert pesticide ingredients.⁷¹ We believe this is good news for public health and hope the agency is successful in finalizing that action.

Adjuvants. The US federal government does not regulate adjuvants as pesticides.⁹ If an adjuvant product is to be used on food crops, its ingredients may require a tolerance or exemption

from a tolerance under the Federal Food, Drug and Cosmetic Act (FFDCA), but there is very little federal oversight.⁷²

Some US states regulate adjuvant products. The most robust system is in California, which requires adjuvants to be registered as pesticides, submission of formulation information, and reporting of adjuvant use.^{9,73} Adjuvants are widely used in California: Forty-one of the most widely applied 100 pesticide ingredients

Table 3. A list of organofluorine and PFAS inert ingredients approved in the United States and Canada and the number of registered products that contain them.

CAS No.	Ingredient name ^a	PFAS	Food use	Approved in the USA	Approved in Canada	Products in the USA (n)	Products in Canada (n)
75-37-6	1,1-Difluoroethane	N	Y	Y	Y	67	3
811-97-2	1,1,2-Tetrafluoroethane	Y	Y	Y	Y	37	15
9002-84-0	Polytetrafluoroethylene (PTFE; Teflon)	Y	Y	Y	Y	14 ^b	2
29118-24-9	<i>trans</i> -1,3,3,3-Tetrafluoroprop-1-ene	Y	Y	Y	Y	3	20
188027-78-3	5H-1,3-Dioxolo[4,5-f]benzimidazole, 6-chloro-5-[(3,5-dimethyl-4-isoxazolyl)sulfonyl]-2,2-difluoro	Y	N	Y	N	0	NA
24937-79-9	Ethene, 1,1-difluoro-, homopolymer	N	N	Y	N	0	NA
42557-13-1	Poly(oxy(methyl(3,3,3-trifluoropropyl)silylene)), alpha-(trimethylsilyl)-omega((trimethylsilyl)oxy)-	Y	N	Y	N	0	NA
593-70-4	Fluorochloromethane	N	N	Y	N	3	NA
63148-56-1	Siloxanes and silicones, Me 3,3,3-trifluoropropyl	Y	N	Y	N	1	NA
67786-14-5	2-Naphthalenesulfonic acid, 6-amino-4-hydroxy-5-{{2-(trifluoromethyl)phenyl}azo}-, monosodium salt	Y	N	Y	N	0	NA
88795-12-4	1-Butanol, 4-(ethoxyloxy)-, polymer with chlorotrifluoroethene, (ethoxyloxy)cyclohexane, and ethoxyethene	Y	N	Y	N	0	NA
98-56-6	Parachlorobenzotrifluoride	Y	INO	N	Y	NA	1
65530-85-0	Alpha-(cyclohexylmethyl)- omega-hydro-poly (difluoromethylene)	Y	INO	N	Y	NA	1
131324-06-6	PTFE, alpha-chloro-omega-(1-chloro-1-fluoroethyl)-	Y	INO	N	Y	NA	1
163440-89-9	PTFE, alpha-hydro-omega-(2,2-dichloro-2-fluoroethyl)-	Y	INO	N	Y	NA	1

Note: CAS, Chemical Abstracts Service; INO, information could not be obtained; Me, methyl; N, no; NA, not applicable; PFAS, per- and polyfluoroalkyl substances; Y, yes.

^aData in this table were obtained through database searches, personal communications, and public records requests.^{31–33}

^bAfter formally responding that 14 products contained PTFE, the US EPA has since publicly stated that zero products contain PTFE and has proposed to remove it from the list of approved inert ingredients in the United States.

are adjuvant ingredients.⁷⁴ The high use of these ingredients indicates that they may be a source of PFAS contamination in the environment.

The only sources of information on adjuvant ingredients we found came from the agrochemical industry and the few state-level agencies in the United States that regulate them. The industry views this information as proprietary, so publicly available information is scant. TELUS, a producer of agricultural industry software, maintained a label database³⁴ that at our date of search encompassed 1,343 adjuvant products. An advanced search for “adjuvant” products containing active ingredients with the term “fluoro” returned zero results. However, it was unclear whether all ingredients were disclosed on this database and whether full chemical names were listed.

We also received public records from California and Washington State. An inquiry to the California Department of Pesticide Regulation (CDPR) asking whether any adjuvants contained fluorinated ingredients elicited the response that “there are no adjuvant products currently registered by DPR which contain fluorinated chemical ingredients.”³⁵ In 2020, the Washington State Department of Agriculture developed a list of spray adjuvant ingredients that identified 313 ingredients in state-registered adjuvant products.³⁶ The Washington State Department of Agriculture requires only the top three ingredients in adjuvant products to be disclosed to the state,⁷⁵ and our search of this partial ingredient list identified no fluorinated ingredients.

Although we found no evidence to indicate that adjuvant products contained fluorinated ingredients or PFAS, our dataset was incomplete and regional, and we concluded that it does not provide strong evidence that no adjuvant ingredients are fluorinated. Rather, the lack of transparency and oversight of adjuvants meant that a robust dataset was not available.

Unintentional addition of PFAS. Leaching from storage containers. The practice of fluorinating polyethylene plastic containers to prevent permeability of aromatic chemicals started as early as 1958.⁷⁶ Today hundreds of millions of high density polyethylene (HDPE) containers that contain agricultural products, personal care products, household cleaning supplies, home improvement products, and food are fluorinated each year.⁷⁷ The most common method of fluorinating hydrocarbon-based plastics is post-mold fluorination,⁷⁸ where already molded containers are treated with fluorine gas under high temperature and pressure.

The goal of post-mold fluorination is to swap out the carbon–hydrogen bonds of the HDPE to carbon–fluorine bonds in a thin layer on the surface of the plastic to enhance its barrier properties. If there is any oxygen or water in the fluorination chamber, then the fluorination process will form perfluorinated structures.

In 2011, researchers discovered that a subset of PFAS, perfluorinated carboxylic acids (PFCAs), were formed during the direct post-mold fluorination of HDPE containers when trace amounts of oxygen were present.⁷⁷ Eight years later, Public Employees for Environmental Responsibility (PEER) discovered that the insecticide Anvil 10+10 contained perfluorooctanoic acid (PFOA) and hexafluoropropylene oxide dimer acid (HFPO-DA).⁷⁹ This finding spurred the US EPA to test the leaching potential of fluorinated HDPE containers that were used to store pesticides, and the agency identified eight PFCAs leaching from various containers—with total concentrations in the 10–60 ppb range.⁸⁰ The US EPA’s findings that fluorinated HDPE containers leach PFCAs has been reproduced by other groups and is now a well-established contamination pathway for contents stored in these containers.⁸¹ It is estimated that 20%–30% of all hard plastic containers used in the agricultural sector are fluorinated,⁸² elevating concerns about widespread PFAS contamination.

Since PEER’s initial testing of Anvil 10-10 found PFAS, many other groups have tested and found long- and short-chain PFAS in multiple pesticide products in a manner that is consistent with container leaching (Table 4). It should be noted that the results of this testing by different groups have produced conflicting results that appear to depend on the analytical methodology used and where the testing was conducted, affirming the difficulty of testing complex mixtures such as pesticide products for PFAS.

In late 2023, the US EPA used its authority under the Toxic Substances Control Act (TSCA) to prohibit the production of multiple PFAS in the container fluorination process.⁸³ Although we believe this strong action would have been an enormous benefit for public health, the US EPA’s action was overturned by a federal appellate court, and it is unclear whether the agency will pursue further action under a different legal mechanism.⁸⁴

Other potential sources. Although leaching of PFAS from fluorinated containers appears to be the primary contamination pathway of long- and short-chain PFAS into pesticide products, the testing that has been conducted to date indicates there are other sources of contamination. Multiple groups have found that some pesticides contain perfluorinated sulfonic acids (PFSAs) (Table 4). As mentioned above, container fluorination has only been demonstrated to generate PFCAs that are available for leaching.⁸⁰ Therefore, the presence of PFSAs in some products—none of which were approved active or inert ingredients (Table 3; Excel Table S1)—indicates that there are other sources of unintentional contamination.

A recent study on serum levels of long-chain PFAS found that both PFSAs and PFCAs were significantly higher in female Danish greenhouse workers compared with a female Danish urban population measured during the same time period.⁸⁵ The authors concluded that this disparity was likely due to differences in exposure to agricultural pesticide formulations and proposed that pesticides may be an important source of long- and short-chain PFAS exposure to agricultural workers.

More research is needed to examine other potential sources for introduction of long- and short-chain PFAS into pesticide products. It is possible that the solvents or other components used in the preparation of some pesticide products could unknowingly be contaminated with PFAS.

Manufacturing by-products and impurities are another potential source of PFAS in pesticides. US EPA regulations allow pesticide products to contain impurities as long as they are <1,000 ppm and not of “toxicological significance.”⁸⁶ Toxicological significance is defined with regard to impurities that also happen to be known pesticides⁸⁶; however, its meaning is not formally defined for other impurities. The US EPA views any concentration of an impurity meeting the agency’s PFAS definition as toxicologically significant, requiring disclosure.⁸⁷ Yet it is unclear whether this reporting requirement is known among the industry or whether companies even know about PFAS impurities in their products, given that many pesticide products contain undisclosed PFAS ingredients (Table 4).⁸⁸

Consequences of PFAS in Pesticides

In addition to documenting sources of PFAS in pesticide products, we sought to understand how PFAS in pesticide products could be impacting human and environmental health in the United States and beyond. Although a lot of knowledge gaps still exist, the available data are cause for concern. It is our view that PFAS in pesticides, particularly PFAS active ingredients, may be having unintended impacts on environmental and public health that must be mitigated or eliminated to prevent irreversible impacts. Below are examples of potential impacts we have identified.

Immunotoxicity. The immune system is highly vulnerable to exposure to chemical toxicants, particularly during development

Table 4. Compilation of studies analyzing long- and short-chain PFAS detections in pesticide products, estimated PFAS concentration found, where the products were tested, and the analytical methodology used.

Date	Product name	US EPA registration no.	PFAS found	Estimated concentration or range	Samples tested (n)	Where tested	Analytical method used
27 August 2020 ³⁷	Anvil 10-10	8329-62	Perfluorooctanoic acid (PFOA) Hexafluoropropylene oxide dimer acid (HFPO-DA)	ND–250 410–500 ng/L ng/L	2	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
15 September 2020 ³⁸	Anvil 10-10	8329-62	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
23 October 2020 ³⁹	Anvil 10-10	8329-62	HFPO-DA	ND–260	2	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
19 November 2020 ⁴³	Anvil 10-10	8329-62	Perfluorobutanoic acid (PFBA) Perfluoropentanoic acid (PFPeA) Perfluorohexanoic acid (PFHxA) Perfluorohepanoic acid (PFHpA) Perfluorohexanesulfonic acid (PFHxS) 1H,1H,2H,2HPerfluorooctanesulfonic acid (6:2FTS)	52.8–716 35.2–296 17.6–132 ND–53.4 ND–59.2 ND–31.6 ng/L ng/L	9	Alpha Analytical	Modified US EPA method 533
19 March 2021 ⁴⁰	Permanone 30-30	432-1235	PFOA HFPO-DA PFHxA PFHpA PFHpS HFPO-DA Perfluorooctanesulfonic acid (PFOS)	3,500 630 530 270 390 1,200 0.25 ng/L ng/L ng/L ng/L ng/L ng/g	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
13 May 2021 ⁴¹	Frontline Plus for dogs	63331-5	PFHxA PFHpS HFPO-DA Perfluorododecanesulfonic acid (PFDoS)	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
Seresio Collar	11556-155	ND	NA	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)
21 October 2021 ⁴⁴	Permanone 30-30	432-1235	NA	NA	6	US EPA–Fort Meade	Modified US EPA method 537.1 (oily matrix)
PermaSease 30-30	53883-459-86291	ND	NA	NA	1	US EPA–Fort Meade	Modified US EPA method 537.1 (oily matrix)
Malathion 5EC	19713-217	PFOA PFHpS PFBA	510 680 1,500 ng/L ng/L ng/L	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Oberon 2SC	264-719	NA	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Intrepid 2F	62719-442	Perfluorobutanesulfonic acid (PFBS)	350 ng/L	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Ultra-Pure Oil	69526-5-499	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Avid 0.15 EC	100-896	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Pedestal	53883-419-59807	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Ortho Home Defense	239-2717	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Triazicide granules	9688-250-8845	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	
Marathon 1% granular	59807-15	ND	NA	1	Eurofins Lancaster	Modified US EPA method 537 (537 IDA)	

Table 4. (Continued)

Date	Product name	US EPA registration no.	PFAS found	Estimated concentration or range	Units	Samples tested (n)	Where tested	Analytical method used
18 May 2023 ⁴⁵	AVID 0.15 EC	NP	ND	NA	NA	2	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Pedestal	NP	ND	NA	NA	2	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Ultra-Pure Oil	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Marathon 1%	NP	ND	NA	NA	2	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Oberon	NP	ND	NA	NA	2	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Malathion 5EC	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	BotaniGard 22WP	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Overture 35WP	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	Conserve	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327
	XXpire	NP	ND	NA	NA	1	US EPA–Fort Meade	Two modifications of SW846 test method 8327

Note: EPA, Environmental Protection Agency; IDA, isotope dilution anion (exchange solid phase); NA, not applicable; ND, not detected; NP, not provided; PFAS, per- and polyfluoroalkyl substances.

and in older adults.⁸⁹ Long- and short-chain PFAS that have been extensively studied—such as PFOA, PFOS, and perfluorohexane-sulfonic acid (PFHxS)—are known to harm the immune system, weaken the antibody response to vaccinations, and increase the risk of infectious disease.^{90,91} Studies of impacts on the immune system indicate that it is one of the most sensitive targets of PFAS exposure,^{23,92} and both the US EPA and the European Food Safety Authority (EFSA) have identified immunotoxicity as the most potent adverse effect to humans from exposure to certain PFAS.⁹⁰ Given the documented sensitivity of the immune system to PFAS exposure, and that immunotoxicity studies are commonly waived during pesticide registration reviews,⁹³ our analysis focused on this specific health end point. However, we note that with the myriad health effects linked to PFAS exposure, other health end points will likely be of additional interest with regard to fluorinated pesticides.

In 2007, following recommendations from the National Research Council and the US EPA's Science Advisory Panel,⁹⁴ the US EPA required all pesticide active ingredients to be subject to T cell–dependent antibody response testing—which the agency uses as a surrogate for immunotoxicity in general.⁹⁵ Six years after imposing this requirement, the pesticide industry requested that the US EPA conduct a retrospective analysis of the usefulness of the immunotoxicity assay in pesticide registration decisions.⁹⁶ In its 2012 analysis, the US EPA found that, of a representative sample of 155 pesticides that had immunotoxicity testing, the agency only considered 15 (10%) to be immunotoxic.⁹⁶ The US EPA's analysis further found that the 15 immunotoxicity findings did not influence the outcome of the pesticides' risk assessment. Following this analysis, the US EPA indicated that it would be receptive to waiving immunotoxicity studies for pesticide active ingredients.⁹⁶ Reflecting this position, between 2012 and 2018, the US EPA granted 223 of 229 waiver requests (97%) for immunotoxicity testing of pesticide active ingredients.⁹³

However, lost in the US EPA's retrospective analysis, conducted before much of the public or regulatory awareness of the health risks of PFAS, was the fact that 7 of the 15 immunotoxic active ingredients (47%) were organofluorines and 6 of 15 (40%) were PFAS.⁹⁶ That compares with 20% and 13% of conventional pesticide active ingredients that were respectively organofluorines or PFAS as of 2012 (Excel Table S3). Immunotoxic effects have also been reported in the peer-reviewed literature for several fluorinated pesticides, including bifenthrin, fipronil, flupyradifurone, and flonicamid.¹⁰

Troublingly, the number of active ingredients that are fluorinated or that meet the definition of PFAS has increased considerably from 2012 to the present (Figure 1)—the very time period that the US EPA granted 97% of waiver requests for immunotoxicity study requirements.⁹³ This suggests that fluorinated or PFAS active ingredients may be more likely to be immunotoxic than other types of active ingredients and that any associated immunotoxicity may not be accounted for owing to the lack of requirement for scientific study.

Environmental fate. All PFAS contain perfluoroalkyl moieties that are highly stable in the environment.¹⁶ Even a single $-\text{CF}_3$ or a difluoromethylene $(-\text{CF}_2)$ moiety in a pesticide active ingredient can resist degradation under highly stringent conditions.⁹⁷ This all but assures that most PFAS molecules will persist in the environment in perpetuity or break down into a degradate that will similarly persist in perpetuity.¹⁶

This makes it particularly important to fully understand the metabolic life cycle of fluorinated pesticides *in vivo* and in the environment. For example, highly persistent, fluorinated degradates of the PFAS pesticide fipronil are often found at much higher

concentrations in human serum, plasma, and urine^{98–100} and are widespread in the environment.^{101,102} These fluorinated degradates are also more persistent¹⁰³ and more toxic to a wide range of taxa, including mammals, than the parent pesticide ingredient.^{100,104,105} Therefore, a faithful accounting of the pesticide degradates that form within organisms and in the broader environment is essential for proper risk evaluation, particularly for degradates that are highly persistent.

In assessing risk to humans and the environment from the use of a pesticide, the US EPA will estimate exposure to the parent active ingredient and some of its degradates. Which degradates to analyze in the risk assessment is determined via multiple degradation studies—often hydrolysis and photodegradation studies to understand abiotic breakdown and biotic metabolism studies in the terrestrial and aquatic environment.¹⁰⁶ According to US EPA guidelines, the suggested duration of these degradation experiments range from 5 to 30 d for the abiotic degradation studies^{107,108} and 100 to 120 d for the biotic metabolism studies.^{109,110}

Analyzing the degradation of a chemical over the span of 1–4 months gives the risk assessor an incomplete picture of chemical transformations that happen months or years later. For persistent pesticides and those with persistent degradates, there can be significant uncertainty around what the intermediate and terminal degradates are and how long it takes for terminal degradates to form.^{111,112} Current test guidelines were not designed with highly persistent substances in mind, and test duration is specifically cited as one way that limits our understanding of how chemical metabolism proceeds from the parent molecule to its terminal degradates.^{113,114}

Even known highly persistent degradates are sometimes omitted from US EPA risk assessments of active and inert pesticide ingredients. The US EPA will often identify which degradates are of toxicological concern either by assessing the acute toxicity of the degradate(s) or conducting a quantitative structure activity relationship to predict toxicity to certain taxa.¹¹⁵ However, this practice can end up essentially ignoring the release of highly persistent chemicals into the environment. For example, with the PFAS active ingredient sulfoxaflor, the US EPA found that highly persistent fluorinated degradates were expected to contaminate ground and surface water; however, it concluded that the only chemical relevant to assessing ecological risk was the parent molecule because the other degradates were less acutely toxic to aquatic organisms.¹¹⁶ Similarly, the US EPA conducted a quantitative structure activity relationship for the fluorinated degradates of the PFAS active ingredient bicyclopyrone and determined that the only chemical of ecotoxicological concern was the parent molecule.¹¹⁷

The persistence and toxicity of degradates are rarely, if ever, accounted for in the approval of fluorinated “inert” ingredients. A public records request for the degradate/metabolite studies reviewed by the US EPA to support the approval or continued approval of five PFAS inert ingredients [Chemical Abstracts Service (CAS) numbers 42557-13-1, 9002-84-0, 63148-56-1, 67786-14-5, and 188027-78-3] returned no relevant records.¹¹⁸

We believe that basing the ecotoxicological relevance of a highly persistent degradate on a limited number of acute toxicity studies or the presence/absence of an active structural site is likely to miss key risks. Pesticide degradates are widespread in the environment¹¹⁹ and, in many cases, are found in concentrations higher than the parent molecule.¹²⁰ There can be serious consequences if the uncertainty involved in a pesticide approval decision ultimately leads to an underestimation of risk coming from pesticide degradates. The generation of fluorinated degradates that have half-lives in the decades or centuries means that any release into the environment will likely be irreversible and

will be of ongoing concern if those degradates are found to be more toxic than previously thought. This has led some researchers to propose introducing new regulatory hazard categories that accurately reflect relative persistence of a chemical and its degradates and that high persistence alone should be a basis for regulation irrespective of the toxicities that have thus far been identified.^{121,122}

Water contamination. Although most PFAS active ingredients (Table 2) have not been monitored for their presence in the environment across the United States, some older PFAS active ingredients have been actively monitored and found throughout the country. Bifenthrin and fipronil, first approved in 1985 and 1996, respectively, are among the most widely detected pesticides in US streams, lakes, and rivers, and both are often found at levels that exceed aquatic safety thresholds.^{101,123–125} In beeswax samples taken from commercial beehives in multiple US states, 98% contained the 1980s-era PFAS pesticide fluvalinate.¹²⁶ The older PFAS pesticides isoxaflutole and penoxsulam, and their fluorinated degradates, have been detected in groundwater near sites where they are used.^{127,128} Despite making up only 1% of the total applied mass of pesticides that are found in California waters, the PFAS pesticides cyhalothrin and bifenthrin account for 90% of the applied toxicity to aquatic life, indicating they are likely having an outsized impact on aquatic health.¹²⁹

To look more generally at the environmental presence of PFAS active ingredients, we compiled and analyzed USGS data that tested for the presence of a wide variety of pesticides in nearly 500 streams across five regions of the United States between 2013 and 2017 (see the “Methods” section for details).⁴⁶ Of the 225 pesticide compounds tested in water samples, 13 were PFAS active ingredients and 16 were their fluorinated degradates (29 total PFAS analytes). Of those tested, 27 PFAS analytes (93%) from 12 PFAS active ingredients were found in US streams (Table 5). Fipronil and isoxaflutole were most prevalent, whereas isoxaflutole and trifloxystrobin were found in the highest concentrations. Only 1 of the 13 tested PFAS active ingredients had >453,000 kg of annual use in US agriculture during the tested time period and many had <45,300 kg of annual use,¹³⁰ indicating that these are not highly used active ingredients relative to many others used in agriculture. This suggests that the prevalence of these fluorinated pesticides and degradates in waterways cannot be explained by high agricultural use alone.

Only 13 PFAS active ingredients—of 66 conventional active ingredients that are currently registered (Table 2)—have been actively tracked in surface water across the United States in recent years, and 12 have been found (Table 5). Nearly all of these 13 tested PFAS active ingredients have been registered for >20 y (Excel Table S3), suggesting that the increase in fluorinated pesticide approvals in recent years (Figure 1) is having unknown consequences with regard to water quality. Because of this, we believe that in-depth, targeted monitoring studies of all PFAS pesticides and their fluorinated degradates in the United States is critical.

Total organic fluorine in the environment. Increasing scrutiny of PFAS contamination of drinking water, and sources for drinking water, has led to increasing research on organic fluorine compounds in the environment and biota. Analytical measurements of PFAS have typically been limited to targeted testing for a few dozen PFAS chemicals. Studies that have done targeted PFAS testing in conjunction with total organic fluorine measurements have found that targeted testing is capturing only a small portion of the total organofluorine load in the environment and biota.¹³¹ Not only have many studies found that levels of total organic fluorine are increasing, but the fraction of samples attributed to unknown organofluorine chemicals is often high and has also been increasing in recent years.^{131–133}

Table 5. PFAS analytes tested in US surface waters by the USGS between 2013 and 2017, how often they were detected, and the maximum concentration identified.

Active ingredient ^a	Fluorinated analyte	Detections (n) ^b	Max conc (ng/L)
Bifenthrin	Bifenthrin	10	10.7
	cis-Cyhalothrin acid ^c	17	961.4
Fipronil	Fipronil	847	61.8
	Desulfanyl fipronil	342	10.6
	Fipronil sulfide	441	10.6
	Fipronil sulfone	754	18.1
	Dechlorofipronil	0	—
	Desulfanyl fipronil amide	29	14.0
	Fipronil amide	762	84.1
	Fipronil sulfonate	8	72.5
Flubendiamide ^d	Flubendiamide	79	148.9
	Deiodo flubendiamide	2	4.9
Fluometuron	Fluometuron	8	229.5
	Hydroxy mono demethyl fluometuron	2	6.4
	4-Hydroxy- <i>tert</i> -fluometuron	1	7.4
	Hydroxyfluometuron	1	3.9
	Demethyl fluometuron	5	5.1
Indoxacarb	Indoxacarb	1	3.4
Isoxaflutole	Isoxaflutole	11	660.1
	Isoxaflutole acid RPA 203328	271	928.4
	Diketonitrile isoxaflutole	496	2,134.90
Lactofen	Lactofen	0	—
Norflurazon	Norflurazon	111	318.6
	Demethyl norflurazon	137	541.8
Novaluron	Novaluron	2	14.5
Oxyfluorfen	Oxyfluorfen	4	70.4
Prosulfuron	Prosulfuron	3	9.5
Tetraconazole	Tetraconazole	56	62.0
Trifloxystrobin	Trifloxystrobin	151	3,670.80

Note: —, not applicable; max conc, maximum concentration detected; PFAS, per- and polyfluoroalkyl substances; USGS, United States Geological Survey.

^aData in this table were obtained from the USGS.⁴⁶

^bThe USGS sampled 482 streams between 4 and 12 times each during the 6-to 14-wk study period. Number of detections denotes the number of times the analyte was detected in a sampling event.

^cAlso a metabolic product of lambda-cyhalothrin and tefluthrin, two PFAS active ingredients that were not monitored by the USGS.

^dFlubendiamide was canceled in the United States in 2016 and is not currently registered.

This indicates that new or unidentified PFAS are increasingly contributing to the overall organofluorine exposure to people and the environment. Increasingly, this unknown total organic fluorine fraction is thought to be coming from short- and ultrashort-chain PFAS,^{134–136} which we have defined as respectively containing 4–5 and ≤ 3 fully fluorinated carbon atoms. Short- and ultrashort-chain PFAS are also generally more difficult to remove from contaminated water sources by commonly used filtration methods, making any resulting contamination potentially more difficult to rectify.^{137,138} Importantly, the presence of ultrashort-chain PFAS in the environment does not correlate well with the presence of long- and short-chain PFAS, indicating that ultrashort-chain PFAS are coming from different sources.^{135,139}

Given that most of the PFAS active pesticide ingredients in the United States contain a $-CF_3$ moiety, it is possible that many of these active ingredients will eventually break down into ultrashort-chain PFAS as their terminal fluorinated degradates. One such degradate is trifluoroacetic acid (TFA), a highly persistent and mobile chemical that is a known water^{135,139} and food¹⁴⁰ contaminant and has been detected in several wildlife species.^{141,142} A study of Norwegian wildlife found TFA to be a major contributor to total organic fluorine levels in animals.¹⁴¹ TFA is abundant in human serum and urine samples,^{143,144} and exposure to people is thought to occur primarily via contaminated drinking water and indoor household dust.¹⁴⁴

TFA is a known metabolic by-product of some fluorinated pesticides,^{24,97} and TFA levels in waterways and food even correlate strongly with pesticide use.^{140,145} Organically grown food has also been found to have lower levels of TFA than food grown with synthetic pesticides.¹⁴⁰ A study by the German Environment Agency found that, when considering the 28 pesticide active ingredients approved in Germany that have a $-CF_3$ group (and could potentially metabolize into TFA), up to 500 metric tons of TFA pollution could be generated annually in the country just from pesticide degradation.¹⁴⁶

With 66 PFAS active ingredients approved in the United States—and the United States having much higher pesticide use than all countries in the European Union combined¹⁴⁷—the potential TFA pollution in the United States coming from pesticides is likely significantly greater than that of Germany. The USGS estimates that anywhere from 10.4 to 15.9 million kg of PFAS active ingredients are used across the United States each year (Excel Table S6)⁴⁷—the vast majority of which contain at least one $-CF_3$ group and could potentially metabolize into TFA or other persistent, fluorinated water contaminants. Given the annual volume of use, pesticide active ingredients have the potential to contribute significantly to the presence of ultrashort-chain PFAS and, by extension, the total organic fluorine load in the environment and biota.

Regulatory Recommendations

- Based on ample research and scientific testing, we believe that post-mold fluorination of plastic containers cannot be done without producing harmful PFAS that are available for leaching. This practice should be discontinued and substituted with other options, such as barrier methods for plastic that do not use fluorine, and possibly in-mold fluorination if it is found not to produce PFAS.
- The United States and other countries must require that all pesticide ingredients, including inerts, and their relative proportions be disclosed on pesticide labels and material safety data sheets. The American Medical Association made this same suggestion nearly 30 y ago in an effort to protect the public, to no avail.¹⁴⁸ It is our view that the pesticide industry should not be allowed to hide behind spurious claims of confidentiality at the expense of the public's knowledge of the potentially harmful chemicals in widely available products.
- Immunotoxicity studies should no longer be waived for fluorinated active ingredients or inerts, and the US EPA should issue a data call-in for any pesticide ingredients that do not have the necessary testing in place.
- All PFAS pesticides, and all intermediate and terminal degradates, must be fully evaluated for environmental persistence, and the most persistent ones, such as broflanilide, should be mitigated heavily and targeted for replacement with nonchemical or less persistent alternatives. This can be modeled after a P-sufficient framework¹²¹ to prevent potential devastating consequences of releasing highly persistent chemicals with no means for recovery.
- The US federal government must expand environmental monitoring and biomonitoring programs to include all PFAS pesticides to gather timely data on their bioaccumulation and their potential impact on human and ecosystem health.
- Once it identifies all terminal and intermediate degradates from PFAS pesticides, the US EPA must assess the cumulative impacts from fluorinated degradates that are common to multiple active ingredients, such as TFA. The US EPA must also assess how the cumulative use of all fluorinated pesticides can impact the total organic fluorine load in the environment and food.

Conclusions

Pesticide products increasingly contain fluorinated ingredients, and this is happening via multiple pathways. A major contributor of long- and short-chain PFAS (>3 fully fluorinated carbon atoms) into pesticide products was through leaching of PFAS from fluorinated containers (Table 4). The polymer PTFE is also an approved inert ingredient in the United States and Canada, but its use currently appears to be limited to about a dozen products (Table 3). The available data also pointed to unknown sources of long- and short-chain PFAS contamination in pesticide products, which have yet to be identified (Table 4).

The biggest contributor of ultrashort-chain PFAS (≤ 3 fully fluorinated carbon atoms) in pesticide products was active ingredients and their degradates (Table 2). Although 23% of US conventional pesticide active ingredients were organofluorines and 14% were PFAS, those percentages jumped to 61% organofluorines and 30% PFAS when looking just at active ingredients approved in the past 10 y (Figure 1). In our review of US EPA risk assessment documents, these PFAS active ingredients are either extremely persistent themselves or break down into intermediate or terminal degradates that are extremely persistent. The majority of PFAS active ingredients contained a single $-CF_3$ moiety and the few that had been monitored are known to pollute waterways across the United States (Table 5; Excel Tables S4 and S5).

We believe these data indicate that some pesticide products contain complex mixtures of ultrashort-chain to long-chain PFAS that are present in parts-per-billion concentrations for some of the long- and short-chain PFAS and up to parts-per-hundred concentrations for some of the ultrashort-chain PFAS active ingredients. The long-term impacts of using mixtures of extremely persistent chemicals on potentially hundreds of millions of acres of US land every year is, to us, a cause for concern. Most, if not all, PFAS in pesticide products or their degradates are going to be chronic persistent pollutants¹⁶ for the foreseeable future of humanity, and their ultimate impact on human and environmental health are largely unknown. Here we have identified steps the US government can take to mitigate potential impacts of fluorinated components in pesticides with the ultimate goal of eliminating or reducing their use altogether.

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