Forever Pesticides

The Increasing "PFAS-ification" of Agrochemicals

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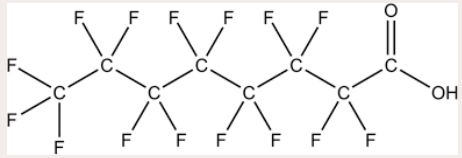
What are PFAS? (and don't tell me "Per- and Polyfluoroalkyl Substances")

"Per- and **P**oly**f**luoro**a**lkyl **S**ubstances" is a general, non-specific term that has been interpreted very differently by many different organizations

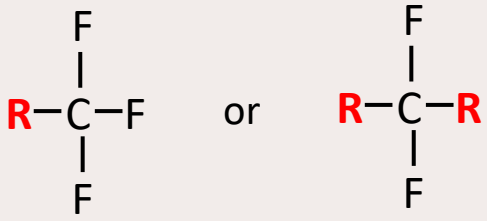
Most people think of PFOA, PFOS, PTFE, GenX…., but the more we're learning about the persistence of organofluorines in general it's clear that we need to be looking at more than just long-chain PFAS



PFOA

There are two main PFAS definitions that are being used in the U.S. right now

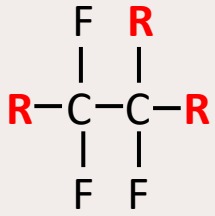
OECD (2021)



Where **R** ≠ H/Cl/Br/I

Used in some states and some other countries

EPA OPPT



Where **R** ≠ H

Used in federal regulation

Why all the fuss?

The carbon-fluorine bond does not exist in nature and no biological processes have evolved to break it down

Therefore, PFAS are all synthetic "forever chemicals" where all or part of the molecule will likely exist for generations or in perpetuity

The few PFAS that have been studied in any depth are known to be harmful to humans and the environment at very low doses

How Do PFAS Get Into Pesticides?

What happens when I add this…

Intentional

- **Active Ingredients**
- **“Inert” Ingredients**

How’d that happen?

Unintentional

- **Container Leaching**
- **As-of-yet unknown Sources**

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What happens when I add this…

Intentional → **Active Ingredients**

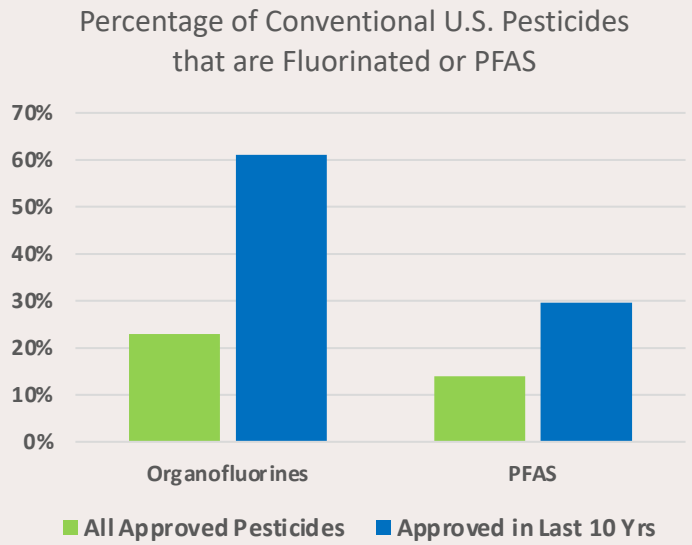
Intentional → "Inert" Ingredients

Active ingredients are the chemicals that kill the targeted pests – the primary constituent in the pesticide

How'd that happen?

Unintentional → Container Leaching

Unintentional → As-of-yet unknown Sources



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In review

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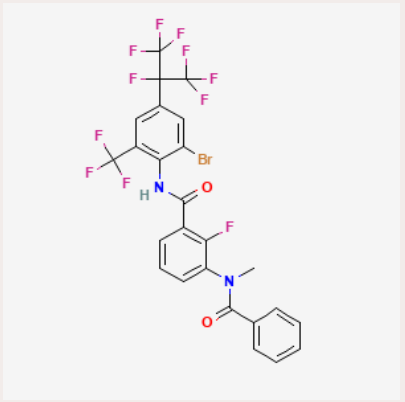
Broflanilide (2021)



Soil half-life >6 yrs

Aqueous half-life 5.5 yrs

Metabolites likely have half-lives on par with DDT

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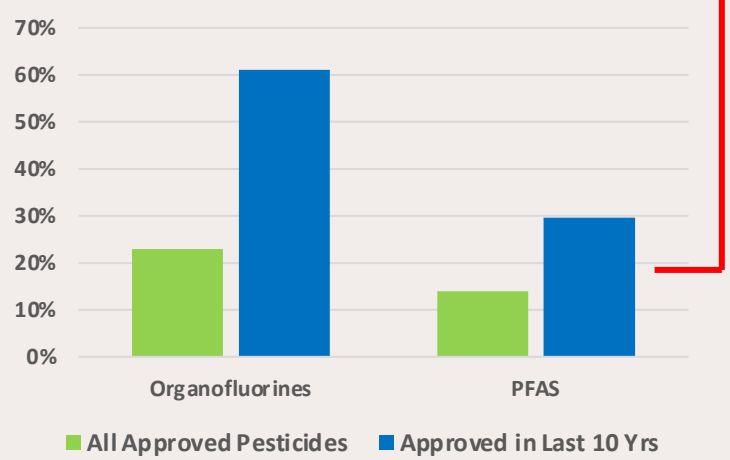
As-of-yet unknown Sources



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“Inert” ingredients are every other chemical in the pesticide product other than the active ingredient. They often account for the bulk of the product

Inerts are often shrouded in secrecy and very little publicly available info exists

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From FOIA we have found that there are 11 fluorinated inerts registered with EPA and 8 are PFAS, including….

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PTFE!!

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On a brighter note, it looks like these PFAS inerts are not present in many products

8 PFAS inerts approved in US are in 55 pesticide products

7 PFAS inerts approved in Canada are in 41 products

We don’t know what these products are, and though the numbers are low, they could be widely-used

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In 2020 PEER found levels of PFOA and GenX in ppt and ppb concentrations in multiple mosquito insecticide products – state of Mass. confirmed

EPA believes this is coming from chemical-resistant containers and confirmed leaching of multiple PFAS from containers – now a well-established pathway for PFAS contamination

Fluorination of rigid plastic containers does not just happen for pesticides, but food containers as well

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Now multiple groups have found ppt and ppb concentrations of long-chain PFAS in many different pesticide products using a 3rd party, certified lab

However, EPA's own testing has failed to reproduce some of these findings

Need to continue to work to standardize valid reliable testing, given the persistent nature of PFAS in pesticides

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The testing that has been done is finding PFAS that are not active or inert ingredients and are also not produced via container leaching. So there appears to be other sources

Possible other sources could be impurities from other ingredients or contamination of solvents like water or oil that are used to formulate the pesticides

Risk Assessment Not Designed with Persistent Chemicals in Mind

- Current EPA guidelines require studies to analyze degradation over 1-4 months. For chemicals or degradates with half-lives in the decades or centuries, this gives an incomplete picture of what these chemicals are transforming into over time
  - ➢ Sometimes even known highly persistent degradates are ignored - ex. sulfoxaflor, bicyclopyrone

- The uncertainty involved in what highly persistent degradates will be formed and where necessitates monitoring….the problem is that's not happening

- One major source of organic fluorine in the environment is trifluoroacetic acid – just so happens to be a degradate of many PFAS actives. But cumulative impact not assessed

# of PFAS active ingredients	66
# monitored in water by USGS	13
# found by USGS	12

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- Any release of highly persistent chemicals 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

Takeaways

> *"If the intent was to spread PFAS contamination across the globe there would be few more effective methods than lacing pesticides with PFAS"*
> – PEER's Science Policy Director Kyla Bennett

- Unintentional contamination, and we assume currently, to a lesser extent "inerts," are the likeliest sources of long-chain PFAS like PFOA, PFOS, and PTFE
- Active ingredients are the major source of ultrashort-chain PFAS (C1-C3) and are present at much higher concentrations. Between 23-35 million lbs of PFAS active ingredients are used each year. Only 20% of PFAS active ingredients have been actively monitored by USGS in water, and many are widely detected
- Whatever is put into our environment today will persist in one form or another for generations
- If the 60s and 70s were the age of the organochlorine (DDT, aldrin, chlordane), we're living in the age of the organofluorine, and the legacy impacts are not well understood