Fluorinated Compounds

Fluorinated Compounds: PFAS Classifications, Definitions and Context with Pesticides

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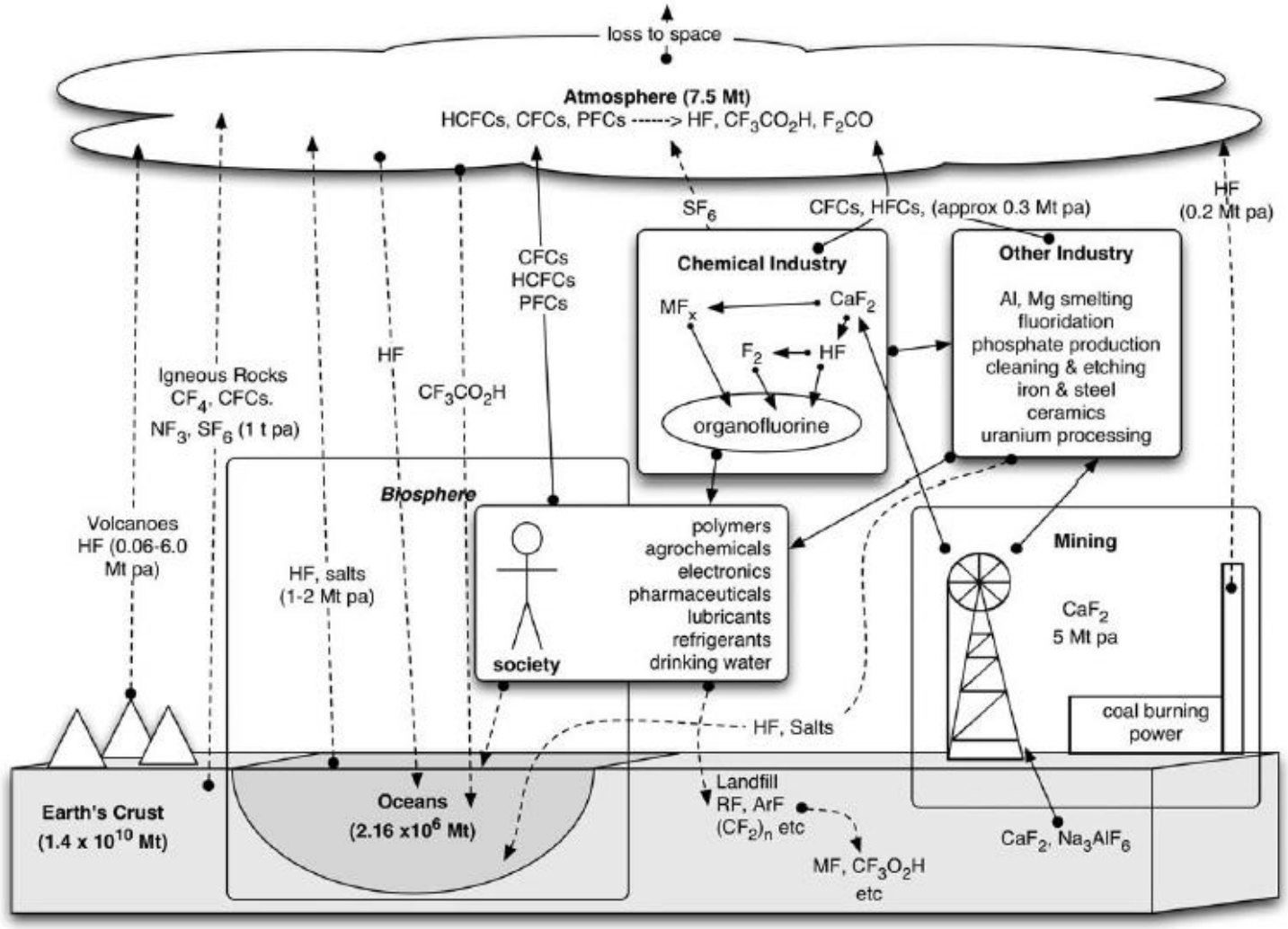
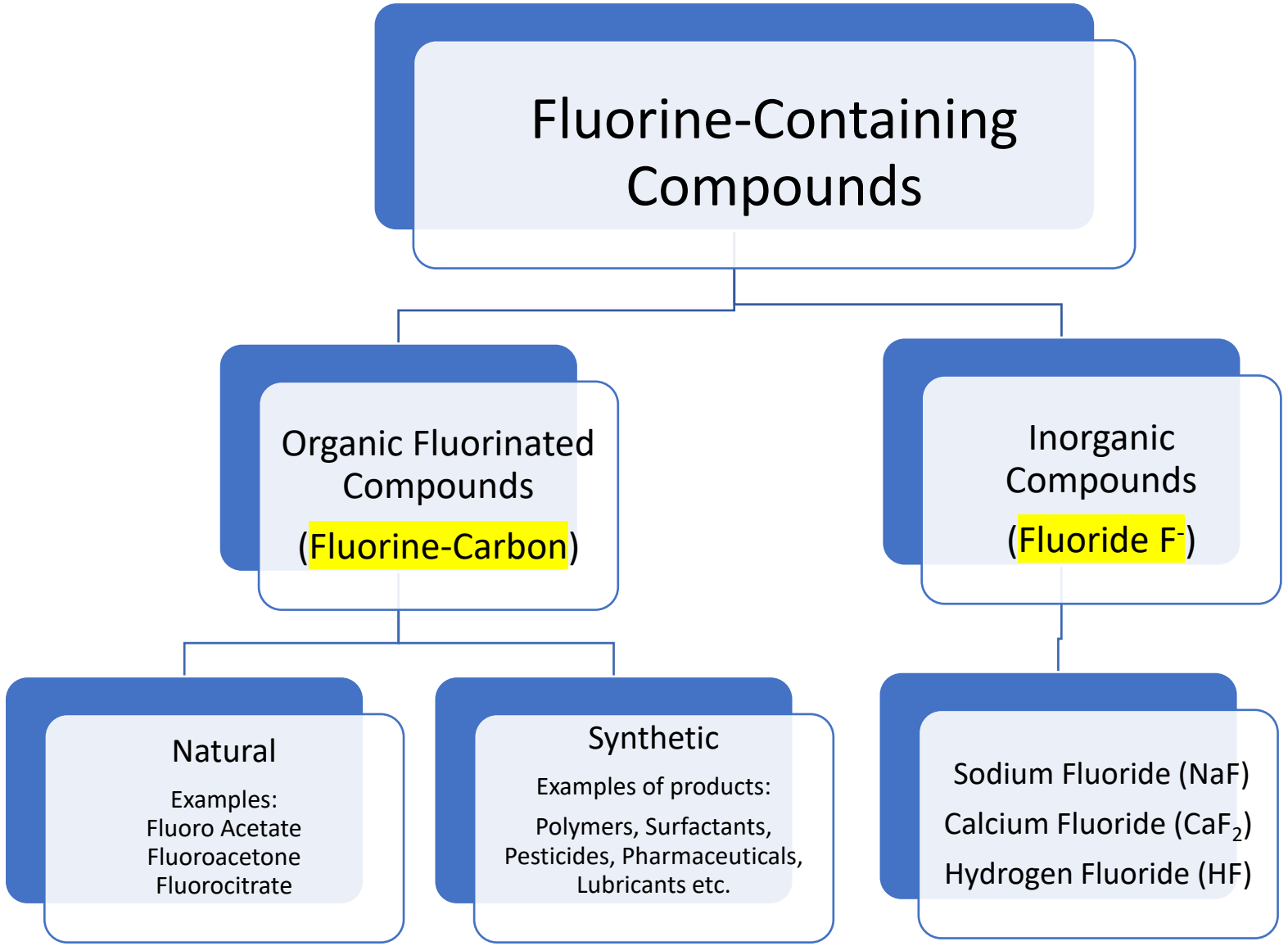
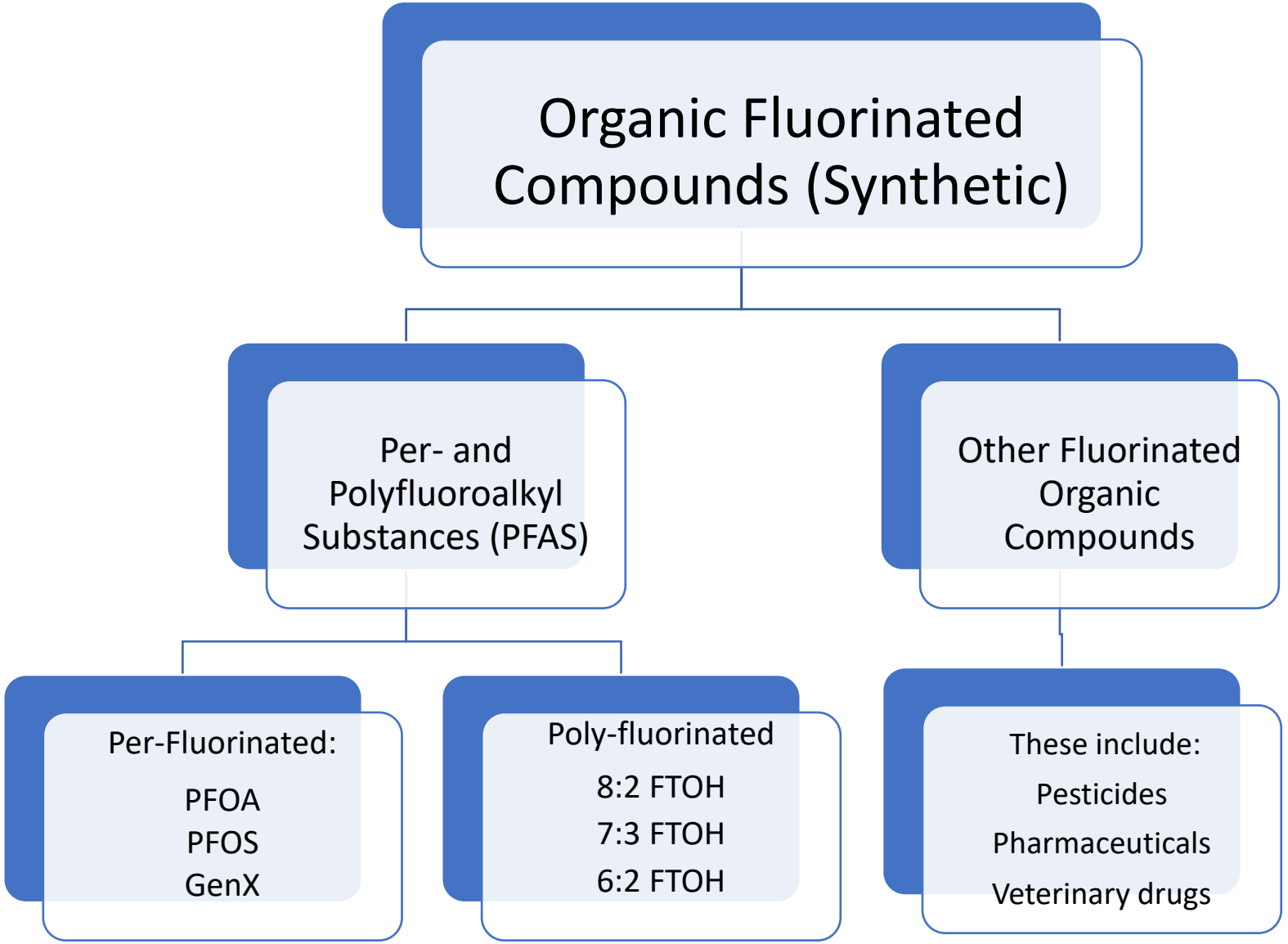
The Fluorosphere: Fluorine reservoirs and fluxes on Earth



Source: Tavener and Clark, 2006. Fluorine: Friend or Foe? A Green Chemist's Perspective
Stewart J. (https://www.elsevier.com/books/fluorine-and-the-environment-agrochemicals-archaeology-green-chemistry-and-water/tressaud/978-0-444-52672-4)


Fluorine-Containing Compounds
Organic Fluorinated Compounds
(Fluorine-Carbon)
Inorganic Compounds
(Fluoride F^-)
Natural
Examples:
Fluoro Acetate
Fluoroacetone
Fluorocitrate
Synthetic
Examples of products:
Polymers, Surfactants, Pesticides, Pharmaceuticals, Lubricants etc.
Sodium Fluoride (NaF)
Calcium Fluoride (CaF_2)
Hydrogen Fluoride (HF)

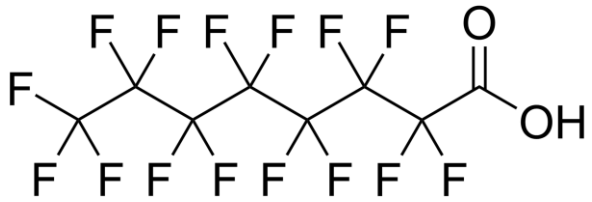


Selected examples mostly based on review by Fiedler et al., 2020 (https://setac.onlinelibrary.wiley.com/doi/full/10.1002/ieam.4352)

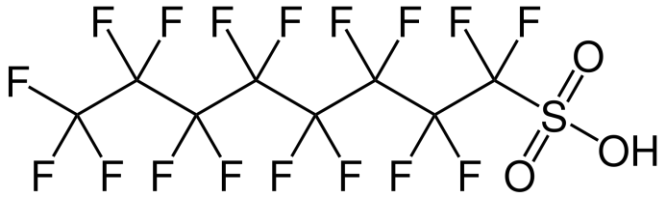
Examples of PFAS Structures

Examples of Per-Fluorinated

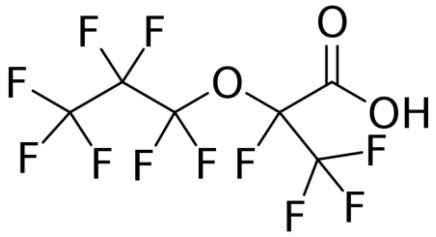
- PFOA



- PFOS

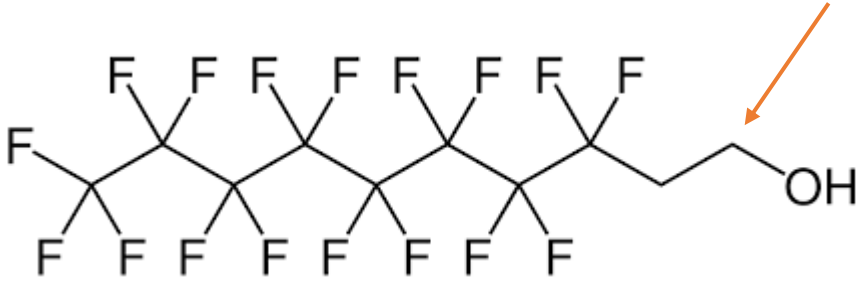


- GenX



Example of Poly-Fluorinated

- 8:2 FTOH



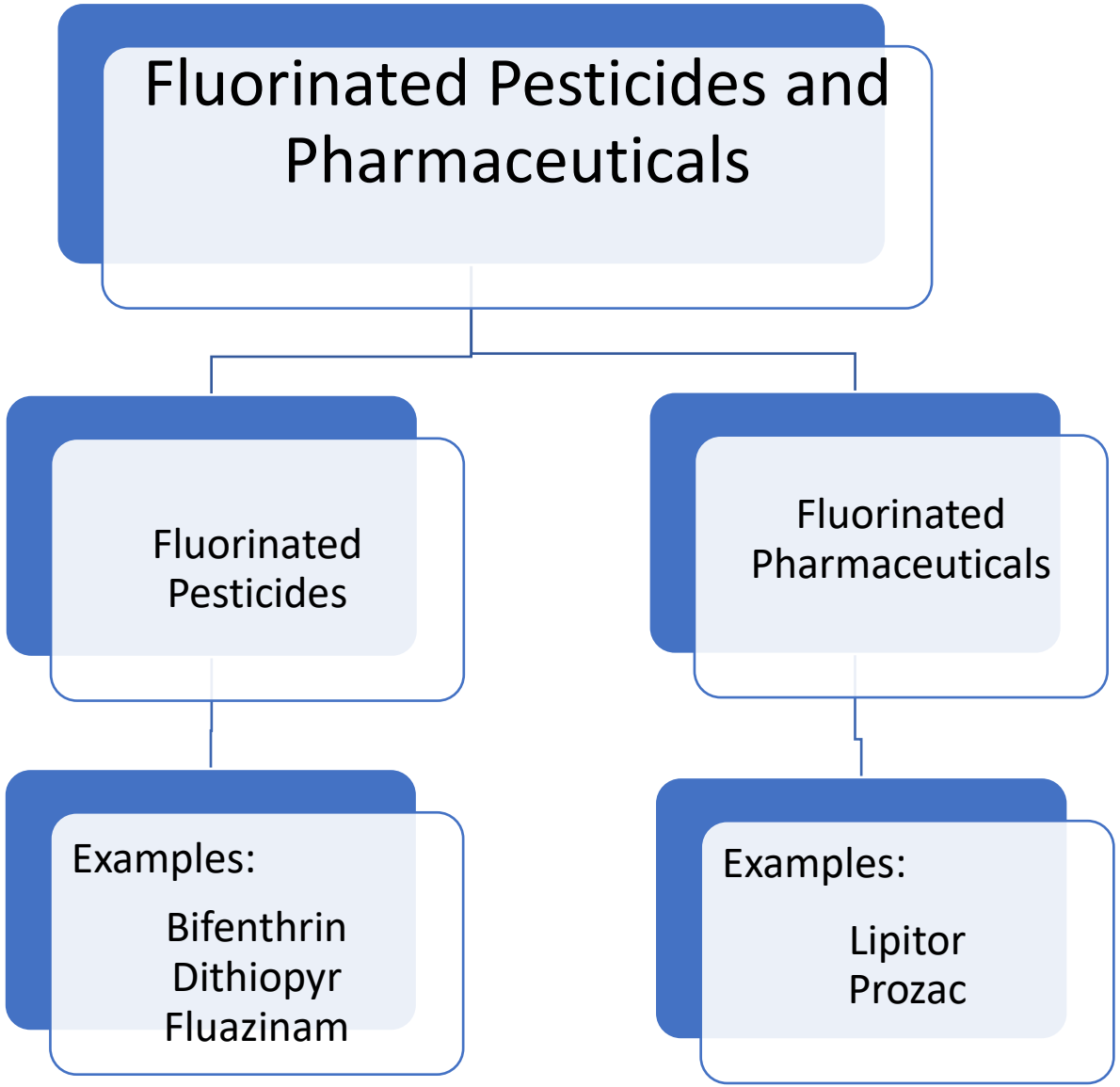
Integrated Environmental Assessment and Management

Critical Review | Open Access

A Critical Review of a Recommended Analytical and Classification Approach for Organic Fluorinated Compounds with an Emphasis on Per- and Polyfluoroalkyl Substances

Heidelore Fiedler, Todd Kennedy, Barbara J Henry

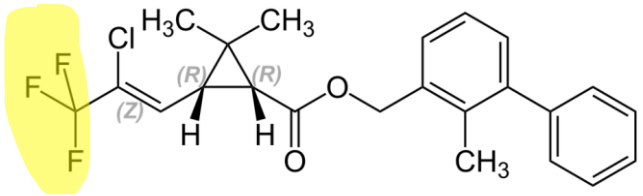
First published: 03 October 2020 | https://doi.org/10.1002/ieam.4352 | Citations: 2


Fluorinated Pesticides and Pharmaceuticals
Fluorinated Pesticides
Fluorinated Pharmaceuticals
Examples:
Bifenthrin
Dithiopyr
Fluazinam
Examples:
Lipitor
Prozac

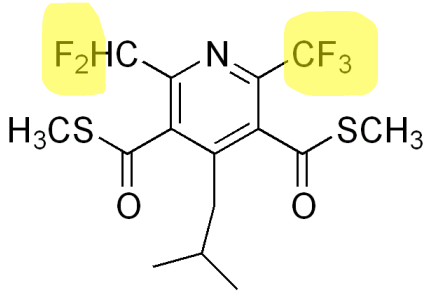
Fluorinated Pesticides and Pharmaceuticals: Structures

Fluorinated Pesticides

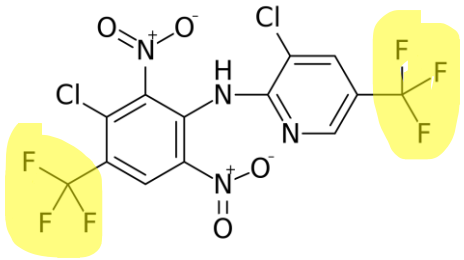
- Bifenthrin



- Dithiopyr

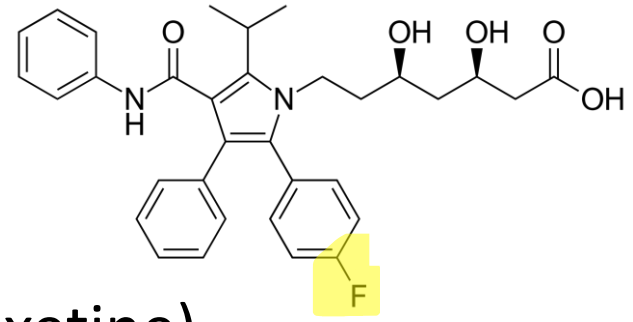


- Fluazinam

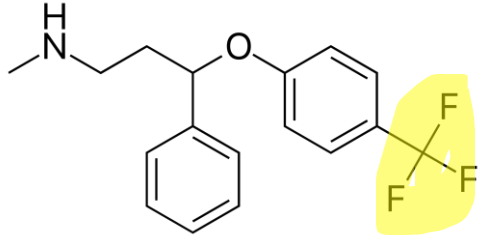


Fluorinated Pharmaceuticals

- Lipitor (Atorvastatin)



- Prozac (fluoxetine)



Comparison of Fluorinated Pesticides with PFASs

Fluorinated Pesticides/Pharmaceuticals	PFASs

• Relatively low fluorine content
• Fluorine atoms or groups located in specific location(s) in molecular structure
• Fluorine contributes as a building element/moiety in the overall molecular design to achieve desired bioactivity, bioavailability, lipophilicity and stability
	• High fluorine atom content
	• Partially to completely saturated with C-F
	• Desired properties derive primarily from fluorinated carbon chains
	• Properties can include:
	  • Persistence
	  • Heat tolerance
	  • Water repellency

PFAS Classifications and Listings

- PFAS classifications consider:
  - Molecular structure, regulatory context and use pattern
  - Various definitions are used across different user groups and programs

- OECD Classification (updated in 2021)*
  - Captures broadness of PFASs and define the PFAS universe
  - Recognizes diversity in structures and vastly different properties
  - Highlights the need to distinguish between the general definition and user-specific working scopes
  - Provides guidance on selecting categories/working scopes for specific activities

* Organization for Economic Cooperation and Development (OECD), 2021. Reconciling Terminology of the Universe of Per- and Polyfl uoroalkyl Substances: Recommendations and Practical Guidance

PFAS Classifications and Listings

- EPA's PFAS Master List of PFAS Substances (~6000 compounds)
  - Inventory of chemicals of interest to the general public, scientific researchers, and regulatory agencies
  - Encompass PFASs of potential interest based on environmental occurrence and manufacturing process data
  - There is no precisely clear definition of what constitutes a PFAS substance based on these lists
  - PFASMASTER serves as a consolidated list of substances, defining a practical boundary of PFAS chemical space of current interest to researchers and regulators worldwide

EPA's PFAS Master List of PFAS Substances: https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster

EPA Office of Pesticides Programs:

PFAS in Pesticides

and

PFAS Working Definition

"There are no pesticide active or inert ingredients with structures similar to prominent PFAS such as PFOS, PFOA, and GenX in currently registered pesticides"

"Further evaluate structures by applying the latest working definition from our sister office, the EPA Office of Pollution Prevention and Toxics (OPPT), which manages the Toxic Substances Control Act (TSCA) program."

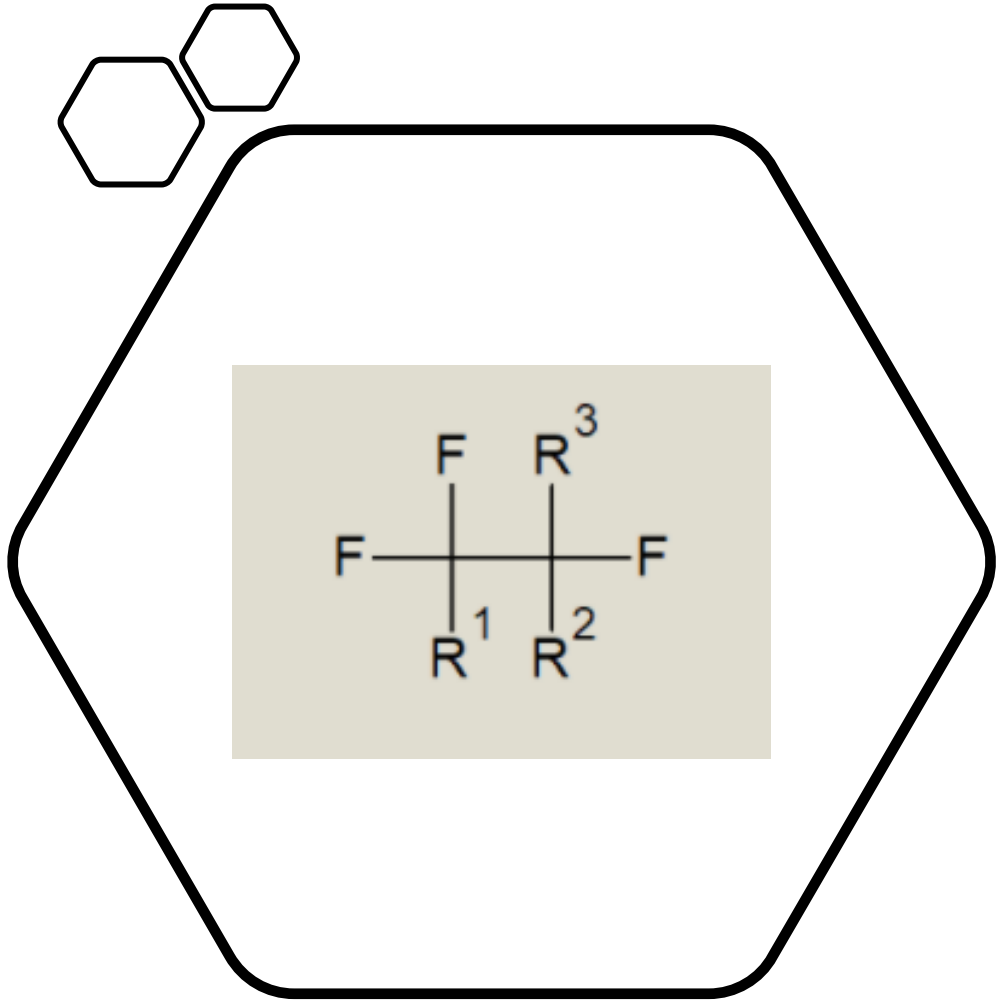
EPA webpage on Per- and Polyfluoroalkyl Substances (PFAS) in Pesticide Packaging

EPA Office of Pesticides Program Working Definition for PFAS

- OPPT applies the following “working definition” when identifying PFAS on the TSCA Inventory:
- A substance that has at least two fluorine atoms on one saturated carbon and at least one fluorine on an adjacent carbon with neither carbon bound to a hydrogen (see structure image),

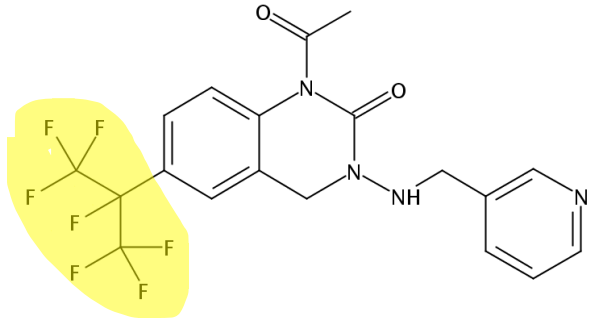
where none of R^1, R^2, or R^3 is H

(https://www.epa.gov/pesticides/pfas-packaging)

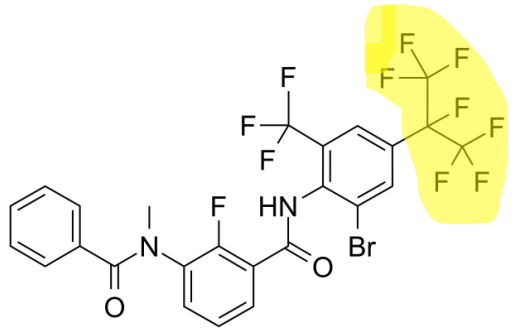


PFAS Working Definition and Registered Pesticides

- One active ingredient registered in Massachusetts that meets the working definition:
  - Pyrifluquinazon (two products registered in MA)



- At least one other active ingredient registered by EPA meets the definition:
  - Broflanilide



PFAS and Pesticides: EPA Responses and Actions

- Pesticide active ingredients that meet the PFAS working definition:
  - Meet FIFRA standards for registration
  - Have undergone the studies, testing and risk assessments that are required for pesticide registration
- Inert Ingredients:
  - There are no PFAS compounds with structures similar to prominent PFASs such as PFOS, PFOA that meet the current working definition in registered products
- EPA's PFAS Action Plan addresses broader PFAS scope (see later slide)

Pesticides used in Mosquito Control

- None of the active ingredients in products used meet EPA's PFAS working definition

- PFASs have been found as contaminants in certain products
  - PFASs detected are compounds with structures similar to prominent PFAS such as PFOS and PFOA that meet the PFAS working definition
  - Contaminants such as these PFASs require registrants report to EPA
  - Based on labeled uses, very small amounts of PFAS were associated with application according to label instructions and do not present a health concern or environmental risk.

- Additional testing by EPA and MassDEP indicated that PFAS contamination originated from containers that undergone fluorination treatment used to coat the plastic containers in which the pesticide was packaged.

Pesticides used in Mosquito Control

Actions taken relative to PFAS Contamination:

- The manufacturer no longer uses Anvil 10+10 packaged in the PFAS contaminated plastic containers and has switched to new containers that are not expected to leach PFAS.
- MassDEP conducted testing on the pesticide from the new containers and confirmed the absence of PFAS
- Testing was conducted on several liquid pesticide products in various containers.
  - If a pesticide product showed measurable levels of PFAS, the mosquito control district stopped using it and chose an alternative that had been tested and did not show measurable levels or switched to a granular product that was packaged differently.
- States and EPA continue to work on the PFAS contamination issue

PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024

- Publish a **national PFAS testing strategy** to deepen understanding of the impacts of categories of PFAS, including potential hazards to human health and the environment. *(expected fall 2021)*
- Ensure a **robust review process for new PFAS** under the Toxic Substances Control Act to ensure these substances are safe before they enter commerce. *(ongoing)*
- **Review existing PFAS** under TSCA to ensure existing PFAS are being used in ways that do not present concerns, and to prevent resumed production of legacy PFAS or their use in new ways. *(expected summer 2022 and ongoing)*
- **Enhance PFAS reporting** under the Toxics Release Inventory by proposing a rulemaking to remove exemptions and exclusions for toxic chemical reporting. *(expected spring 2022)*
- **Finalize new PFAS reporting** under TSCA Section 8 to better characterize the sources and quantities of manufactured PFAS in the United States. *(expected winter 2022)*

More info available at: https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024