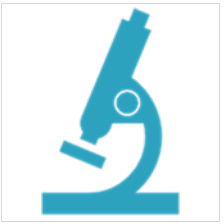
PFAS and Pesticides

Experiences with PFAS Testing in Mosquito Control Products in Massachusetts



Hotze Wijnja
Massachusetts Department of Agricultural Resources

PFAS TSCA Workshop, February 2024

Toxic 'forever chemicals' found in pesticide used on millions of Mass. acres when spraying for mosquitoes

Boston Globe, December 1, 2020

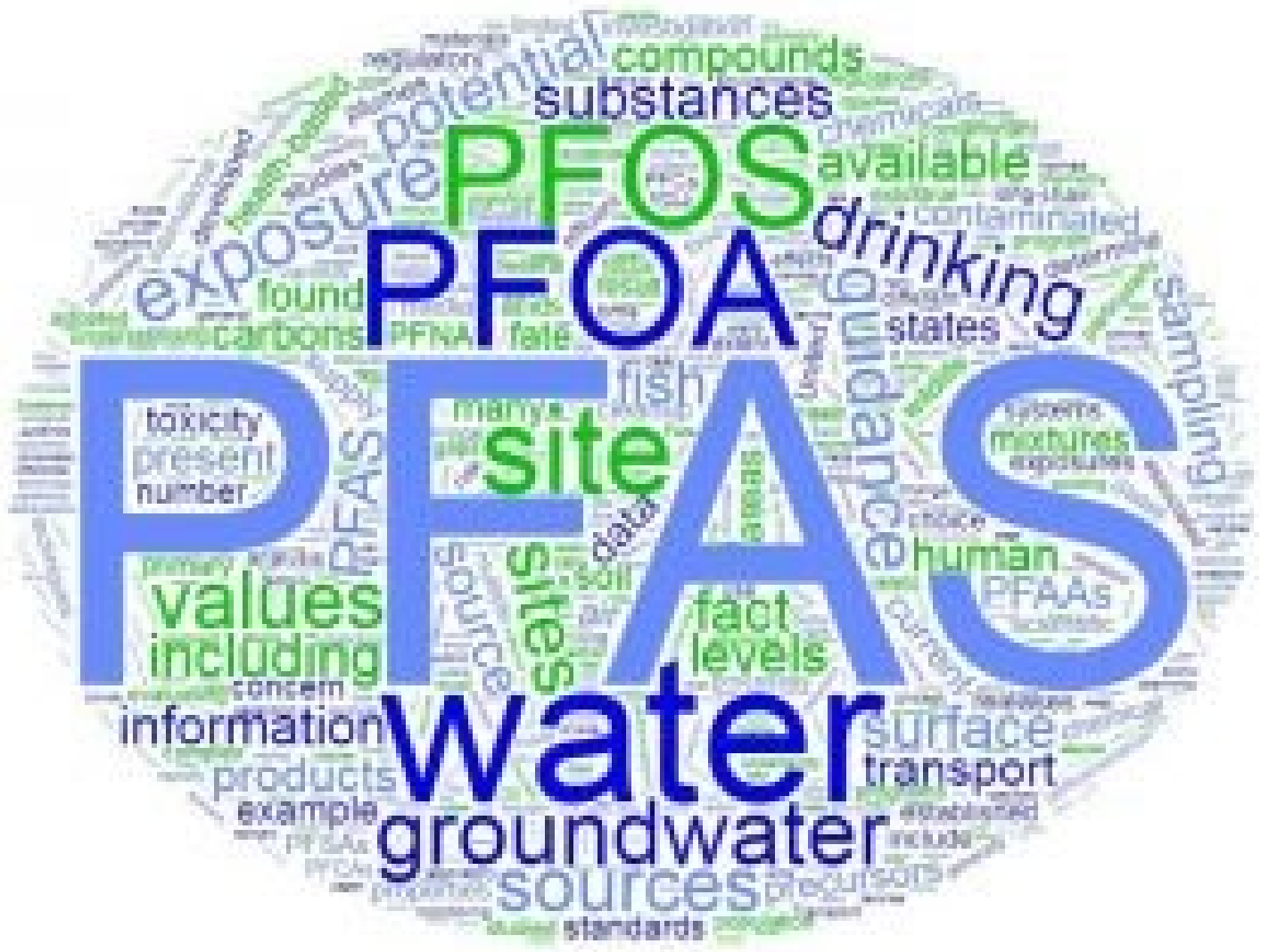
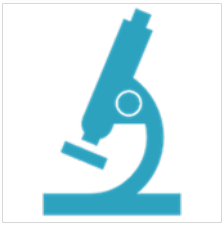
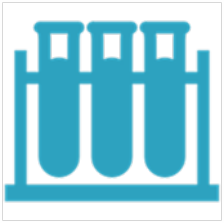


Image from Midwest Environmental Justice Organization

Focus of Presentation



- Highlighting the importance of using proper analytical methods for product testing
  - Context is pesticide products and regulatory program
  - Many pesticide product formulations are complex
  - Sample matrix can interfere with PFAS analysis
  - Existing analytical methods may result in unreliable test data

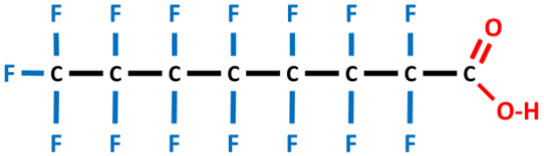


- Challenges for Pesticide Regulatory Programs

Initial Reports of PFAS in Pesticides, 2020

- Public Employees for Environmental Responsibility (PEER) notified MassDEP and MDAR that samples of **Anvil 10+10** (Sumithrin, PBO) contained PFAS
  - Two PFAS compounds (**PFOA, HFPO-DA**) in the range of <250-500 parts per trillion (ppt) (estimated values)

- MassDEP independently tested Anvil 10+10
  - Confirmed the presence of several PFAS compounds



Early Responses to Emerging Issue of PFAS and Pesticides (Anvil 10+10)

- EPA and MassDEP: Followed up with manufacturer and confirmed that no PFAS used in product and manufacturing process
- EPA: Test results of container rinsates suggest that the source of contamination is associated with the fluorinated HDPE containers
- EPA worked with manufacturer to stop shipments of the product in fluorinated containers
- EPA: worked with partners and stakeholders on PFAS and fluorinated containers to raise awareness and encourage product stewardship

See also EPA webpage:
https://www.epa.gov/pesticides/pfas-packaging

Early Responses to Emerging Issue of PFAS and Pesticides (Anvil)

- Winter 2020/2021: Manufacturer switched to all non-fluorinated containers
- MassDEP sampled and confirmed that Anvil 10+10 packaged in new container does not contain measurable PFAS
- Spring 2021 – 2022: MassDEP/MDAR sampled additional mosquito control pesticides
  - Assess the scope of PFAS contamination
  - Several rounds of sampling and testing, including containers

PFAS Testing of Mosquito Control Products

- Spring 2021: (Round 1)
  - Initial sampling of 10 different products (all liquid formulations)
  - Additional sampling to refine the assessments and to follow up on changes in product packaging
- Summer and Fall, 2021: (Round 2)
  - Testing of empty containers and follow- up testing of certain products
- Summer 2022: (Round 3)
  - Additional follow-up testing of certain products

PFAS Testing: Approach and Methodology

- Sampling:
  - types of container & sizes
  - multiple lots of product, if available
  - QA/QC samples (field blanks, equipment blanks, field duplicates)
- "Modified" EPA Method 533 used by contract lab (Isotope dilution, 25 PFAS analytes)
- Manufacturers provided **empty containers** for rinsate testing
- MA agencies shared information with manufacturers

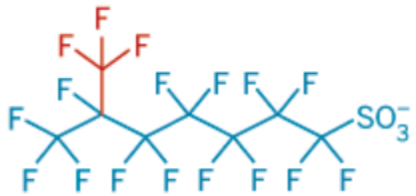
PFAS Test Results: Round 1 2021

- Round 1: March – June of 2021 included 11 different products:
  - **No** measurable PFAS levels (<RLs) in majority of products (7)
  - Four products showed measurable levels (>RLs) of one or more PFAS
    - One BTI larvicide product
    - One Pyrethroid adulticide
    - Two products that were packaged in possibly fluorinated containers:
      - Pyrethroid product: **PFOA** (3,140 ng/L) in one of the two samples
      - Larvicidal Oil: **PFBA** (386 ng/L) in one of the two samples

PFAS Test Results (Round 1)

Round 1 – BTI Larvicide product:

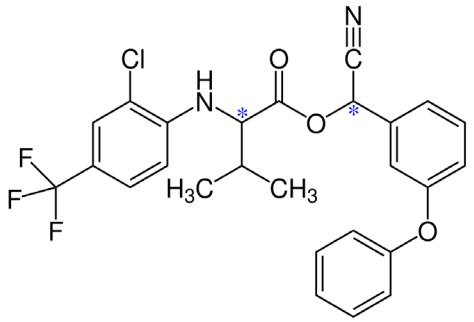
- Packaged in 2.5, 30, 275-gallon containers (all reportedly non-fluorinated); 7 lots sampled
- One PFAS (**PFOS**) detected (RLs = 98–398 ng/L)
  - 2.5 gallon: 3/3 samples > RL; range 2,760 –5,040 ng/L
  - 30 gallon: 12/16 samples > RL; range 2,320 –3,260 ng/L
  - 275 gallon: 0/3 > RL
- Identification of PFOS not certain
  - Possible branched-chain isomers of PFOS ?



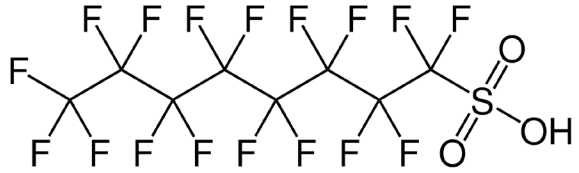
PFOS Branched Isomer (P6MHpS)

PFAS Test Results (Round 1)

Round 1 – Pyrethroid-based product:



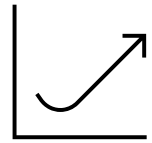
- Two samples (1 lot)
- Measurable PFAS in both samples:
  (RL 98 ng/L)
  - **PFOS** (1,220 – 1,240 ng/L)
  - **PFHpS** (2,060– 2,710 ng/L) and
  - **PFHpA** (297–427 ng/L)



PFAS Test Results (Round 2)

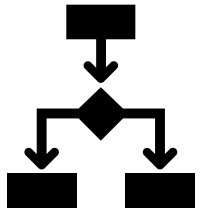
- **Containers Rinsate** tests:
  - **NO** measurable PFAS in 15 out of 17 containers
  - Measurable PFAS in two containers (possibly fluorinated, supply chain mix-up?)
  - Follow up testing of additional product samples showed **NO** measurable PFAS.

- Additional ***pyrethroid product*** testing: (9 samples)
  - Measurable PFAS in all 9 samples (RLs 1750-1960 ng/L)
  - PFAS Sulfonates: **PFOS** (9,190 – 82,500 ng/L); **PFHpS** at 4,980 – 10,400 ng/L; and
  - Various **PFAS carboxylic acids** in several samples in the range of 1,240- 22,600 ng/L



Round 1 and 2: Outcome and Decisions

- Allowed products to be identified that are not expected to contain measurable PFAS

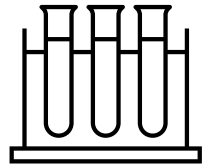


- Two products remained that continued to show measurable PFAS:
  1. *BTI Larvicide product*:
     - Manufacturer demonstrated that bile acid may be present in the product formulation
     - Bile acid confounds PFOS analysis and leads to false positive results if present
     - Analysis using high-resolution mass spectrometry allows differentiation between the bile acid and PFOS

  2. *Pyrethroid product* that showed substantial levels of PFOS, PFHpS and several PFAS carboxylates

PFAS Test Results (Round 3)

- Sample Analysis by Laboratory in Sacramento, CA
  - EPA Method 537 (modified) / (High-resolution MS analysis capability)



- *BTI larvicide*: (RL 100-250 ng/L)
  - No measurable **PFOS**
  - **PFUnA** slightly >RL but considered background and not to be of significance in the context
- *Pyrethroid product*: (RL 2,500 – 11,000 ng/L)
  - No measurable levels of PFAS, but the report identified several analytical issues that were attributed to matrix inferences with the extraction and analysis of the formulated product
  - Reporting limits were relatively high

Follow up

- *Pyrethroid product*: MA agencies were unable to resolve the PFAS testing in this product given the uncertainties
  - Referred to EPA Region 1 for further investigation
  - Work is in progress at EPA to develop an analytical method that is suitable for this type of product formulation
  - Part of ongoing efforts with PFAS analytical method development by EPA [1)]

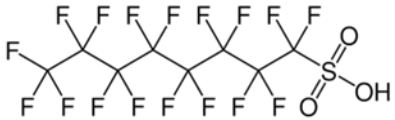
[1)] Per- and Polyfluoroalkyl Substances (PFAS) in Pesticide and Other Packaging: https://www.epa.gov/pesticides/pfas-packaging

PFAS testing of Pesticides by Other Groups

- Example: Study published in *Journal of Hazardous Materials*, November 2022
  - This study reported the presence of **PFOS** in six of 10 pesticide products tested at relatively high levels (ppm)
  - PFOS contamination cannot be linked to fluorinated containers
  - Certain groups even suggest the possibility of PFOS being intentionally added to pesticide formulations

ELSEVIER
Journal of Hazardous Materials Letters
Volume 3, November 2022, 100067

Targeted analysis and Total Oxidizable Precursor assay of several insecticides for PFAS



[1] EPA Completes Scientific Testing of Pesticide Products for PFAS: https://www.epa.gov/pesticides/epa-completes-scientific-testing-pesticide-products-pfas

Pesticide Regulatory Program Challenges

- Calls for taking action to address PFAS contamination in pesticides
  - PFAS testing of pesticide products as part of registration requirement:
    - Physicians for Social Responsibility (PSR), Boston Chapter
      - "We are writing to alert the MDAR Pesticide Board to increasing peer-reviewed scientific data that demonstrate that pesticide products contain PFAS chemicals in extremely high levels, and
      - to urge the Board to use its regulatory authority to take immediate action to protect Massachusetts residents from exposure to PFAS-contaminated pesticides."

Attention and Follow-up in Pesticide Regulatory Community

- EPA conducted a verification analysis of the study published in the *Journal of Hazardous Materials* [1)]
- EPA analysis did **not** find **PFOS** or 28 other PFAS substances in the tested pesticide products
  - EPA evaluated the pesticide products using two different test methods to detect PFAS:
    - A newly developed analytical method to measure specifically PFAS in pesticide samples containing surfactants and non-volatile oils.
    - EPA's method ensures accurate measuring of PFAS by eliminating interference from the oils and surfactants present in these formulations that can result in false positive detections

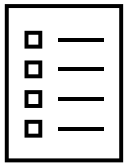
[1)] EPA Completes Scientific Testing of Pesticide Products for PFAS: https://www.epa.gov/pesticides/epa-completes-scientific-testing-pesticide-products-pfas

Summary

- Use of proper analytical method is critical to obtain reliable PFAS testing results
  - Needed to support regulatory programs
  - Few validated methods available for PFAS analysis in pesticide products
  - Use of unvalidated methods results in unreliable PFAS test data being published and used

- Reports on PFAS testing of Pesticides by other groups
  - Typically rely on testing by laboratories using methods that haven't been validated for use in complex samples such as pesticides
  - Results uncertain, including false positives and high report limits

Summary



- PFAS testing in pesticide products is challenging:
  - Different formulations and packaging
  - Analytical challenges and uncertainties
  - Need for validated methods for various formulations
  - Laboratory availability and cost

Thank You!

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