PFAS and Mosquito Control Pesticides in Massachusetts

C. Mark Smith, Ph.D., M.S.
Director, Office of Research and Standards
Massachusetts Department of Environmental Protection
c.mark.smith@mass.gov

Credits

- **MassDEP:** C. Mark Smith; Oscar Pancorbo; Lisa Jordan; Cathy Kiley
- **MDAR:** Taryn LaScola; Hotze Wijnja
- **TRC:** Elizabeth Denly; Yulia Kalmykova
- **EPA, Meade Laboratory**: Thuy Nguyen; Yaorong Qian
- **Alpha Analytical:** Jim Todaro; Jim Occhialini
- **PEER:** Kyla Bennett
- **Manufacturers – Clarke** (Karen Larson; Clark Wood); **Valent** (David Schumacher, Iga Lyczko PhD and Yaohua Wang PhD)

Background: MA Mosquito Control

- Pesticide formulations used for mosquito control are registered by the MA Pesticide Board
  - Based on MA Department of Agricultural Resources (MDAR) review
- Aerial spraying may occur in areas where mosquito-borne disease is deemed to present a public health threat by the MA Department of Public Health (MDPH)
- Mosquito-borne disease concerns
  - Eastern equine encephalitis (EEE)- often lethal
  - West Nile virus
- MassDEP samples surface waters and PWS

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MA Mosquitocide PFAS Timeline

- August 2020: PEER notified MassDEP and MDAR that samples of Anvil 10+10 contained PFAS
  - Mosquito adulticide sometimes used for aerial spraying in MA
  - Last aerial use was in August 2020
- Sept. 2020: MassDEP confirmed PEER's findings
- Possible impact of aerial spray on drinking water sources evaluated
  - Worst case scenario: not detectable/ no risk of exceeding drinking water standards

Timeline Continued

- Manufacturer confirmed that no PFAS used in Anvil 10+10
- Fluorination treatment used to strengthen the containers for safer pesticide shipment and storage identified as potential PFAS source
- December 2020: USEPA reported fluorinated containers leach PFAS using methanol rinsates
  - Duplicate samples provided to MassDEP, similar results
- Winter 2020/2021: manufacturer recalled fluorinated containers
  - Manufacturer switched to all non-fluorinated containers
  - MassDEP sampled and confirmed this Anvil 10+10 does not contain measurable PFAS
- Spring 2021 - present:
  - MassDEP/MDAR sampled additional mosquito pesticides

Possible Sources of PFAS

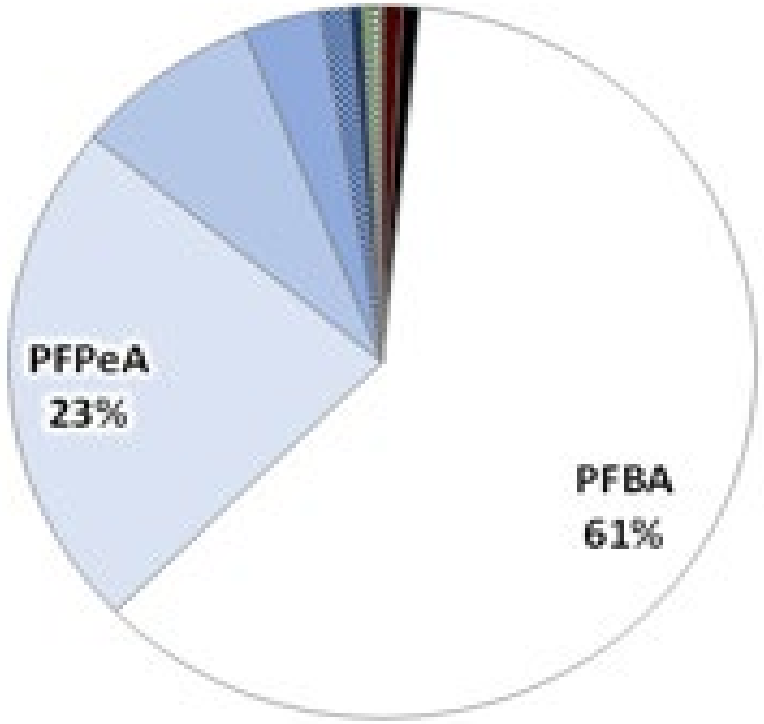
- Intentionally added – possibly used in the past
  - No evidence supporting this possibility now
- Incidental contamination of base ingredients: active agents; surfactants; oils; etc. or of processing equipment
  - No evidence but difficult to rule out
- Containers
  - Fluorination treatment post-manufacture
  - Use of recycled plastics/materials to manufacture containers?

Results For Flourinated Containers

- Significant levels of carboxylates detected in interior and exterior rinsates
- Analytes measured - typically in decreasing order
  - PFBA
  - PFPeA
  - PFHxA
  - PFOA
- Variable concentrations; maximum value 472,000 ng/L for PFBA

Results for Reportedly Non-fluorinated Containers

- Field blanks and 15 of 17 container methanol rinsates below RL (10-17 ng/L) for all 25 Method 533 analytes
- But….PFAS detected in two containers well above RLs



PFAS Target	30-Gallon Rinsate (ng/L)	30- gallon Duplicate Rinsate (ng/L)
PFBA	32,000	39,400
PFPeA	12,200	26,000
PFHxA	4,230	10,700
PFHpA	1,320	3,270
6:2FTS	444	< 500
PFOA	600	1,400
PFNA	280	530
PFDA	204	< 500

Container Rinsate Summary and Conclusions

- Methanol rinsates of fluorinated containers exhibited elevated levels of several PFAS
  - Interiors and exteriors contain methanol-leachable PFAS
  - Primarily carboxylates
  - Concentrations generally inversely related to carbon-chain length
- Two reportedly non-fluorinated containers yielded results consistent with fluorinated containers
  - Possible supply chain mix-up?
  - Possibly some other source?

Uncertainties and Limitations

Methanol rinsates not directly comparable to leaching that might occur in stored formulations

Variations in rinsate procedures likely to impact quantitative results: e.g., repetitive rinsates; volumes of rinsate vs. container surface area; duration; temperature

Some values were estimated by extrapolating well beyond the instrument calibration curve

Other MA Mosquito Pesticide Sampling

- Multiple formulations sampled
- Smaller containers were sampled “shaken (not stirred) and poured”
- Field blanks, equipment blanks, and field duplicates collected
- Opened and unopened containers sampled
- Various types of containers and sizes sampled
- Multiple lots sampled if available

Analytical Method Summary

- No method for PFAS in pesticides at that time
  - EPA Meade Laboratory recently (9/28/21) issued method for PFAS in “oily” substances - https://www.epa.gov/system/files/documents/2021-09/epa-pfas-method-in-oil.pd
- “Modified” EPA Method 533 used by Alpha Analytical
  - Isotope dilution
  - 25 analytes included; MA PFAS 6

MA Mosquitocide Sampling Results

- Measurable levels (>RL) of PFAS were NOT detected in the majority of formulations:
  - Duet; Zenivex E4; Suspend Polyzone and Suspend SC; BVA; Vectobac (265-gallon non-fluorinated containers); Cocobear (non-fluorinated containers); Anvil 10+10 (non-fluorinated containers)
- One or more *putative* PFAS above RLs in five formulations – state ceased use
  - Two from fluorinated containers
  - Three from reportedly non-fluorinated containers; one BTI lavacide formulation) and two synthetic pyrethoid adulticide formulations
  - *Possible* branched chain PFOS detected?

Larvacide Formulation Case - Summary

- 7 lots sampled
  - 2.5, 30, 275-gallon containers (all reportedly nonfluorinated)
- **Possible** branched-chain PFOS in many samples
  - RLs = 98 – 398 ng/L
  - 2.5 gallon: 3/3 > RL; 2,760 – 5,040 ng/L
  - 30 gallon: 12/16 > RL; 2,320 – 3,260 ng/L
  - 275 gallon: 0/3 > RL
- Identification not certain

Larvacide Formulation Case – PFOS or Not?

Some branched isomers of PFOS

		Precursor M_1[a]	Product M_2[a]	Qualifier M_3[a]
Perfluoro-n-octanesulfonic acid	PFOS	499	80	99
Perfluoro-1-methylheptanesulfonic acid	1-PFOS	499	419	
Perfluoro-3-methylheptanesulfonic acid	3-PFOS	499	280	
Perfluoro-4-methylheptanesulfonic acid	4-PFOS	499	230	
Perfluoro-5-methylheptanesulfonic acid	5-PFOS	499	130	280
Perfluoro-6-methylheptanesulfonic acid	6-PFOS	499	80	99

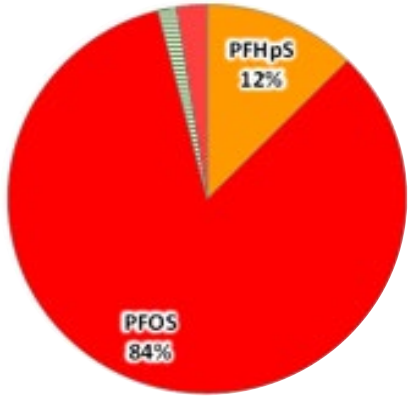
- EPA method monitors PFOS; 6-PFOS M_2 primary ion product
- Secondary (qualifier) ion product not typically assessed but we did for some samples
- Secondary ion for 6-PFOS not detected

Perhaps Not

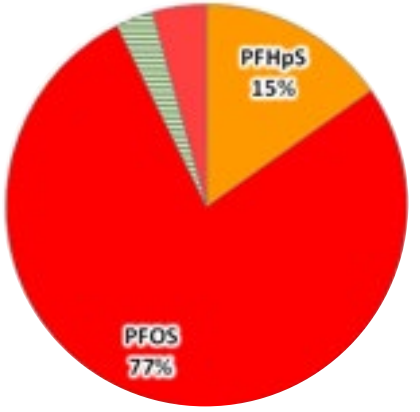
- Manufacturer has demonstrated that bile acids may enter final product
- Bile acids are a known “confounder” in PFOS analysis and can lead to false positive results if present
- This appears to be a likely explanation
- MassDEP conducting additional sampling and analyses to investigate

Synthetic Pyrethroid Formulation Case Summary

- 2 formulations; 8 lots; 11 containers sampled total
- ***All samples with putative sulfonates*** > RL
  - PFOS?: 1,200-82,500 ng/L
    - ?branched chain/bile acid?
  - PFHpS: 2,100 – 10,400 ng/L
  - F-53B: in some up to 2,400 ng/L



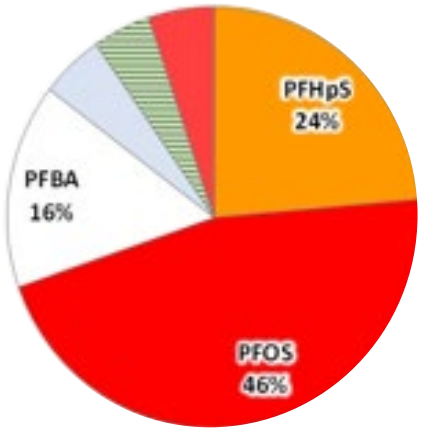
Formulation A
8 oz.
Lot 1



Formulation B
32 oz.

Synthetic Pyrethroid Formulation Case Summary

- *6 lots (7 containers) also with multiple carboxylates*
- *Containers reportedly non-fluorinated but….*
- Profile similar to fluorinated container rinsates
  - PFBA: 4,000 – 22,600 ng/L
  - PFPeA: 2,400 – 13,300 ng/L
  - PFHxA: 2,000 – 9,100 ng/L
  - PFHpA: limited up to 4,300



Formulation A
8 oz.
Lot 3

- MassDEP/DAR analyzing additional samples this spring

Overall Conclusions

- Measurable PFAS unexpectedly detected in some mosquitocide formulations
  - Analytical challenges/uncertainties exist for some data
  - Putative PFOS detection may be spurious
- Because these compounds are persistent, MassDEP and MDAR are committed to identifying and reducing PFAS in pesticides

Overall Conclusions

- Fluorinated containers appear to be a source of PFAS
- PFAS from reportedly non-fluorinated containers suggest supply chain issues or that other sources may be involved
- Agencies are assessing whether fluorinated containers are used for other non-pesticide products
- MA agencies are sharing information with manufacturers, states and other stakeholders

Potential Drinking Water Impacts and 2020 EEE Aerial Spray Event

- Screening assessment using worst-case scenario
  - *maximum total* PFAS concentration detected in any of the samples used (the actual levels were much lower in all)
  - *all* pesticide applied entered water supply (no spraying allowed over reservoirs)
  - *dilution limited* to the top one foot (drinking water supplies much deeper)
  - *no binding to soil or sediments* (this does occur)
  - *PFAS6 RfD used* for all measured PFAS (majority were shorter-chain)
- Conclusion: 2010 Anvil 10+10 aerial application would not have resulted in any detectable PFAS in drinking water or any appreciable risk

Container Sampling Methods

- Preparation of Container Rinsates (U.S. EPA Region 3, Ft. Meade Laboratory, MD) procedure
  - 50 (2.5-gal, 10-L, 8-oz & 16-oz containers) or 300-mL (30-gal, 55-gal, and 114-L) of LC/MS-grade methanol
  - containers capped and manually shaken to allow the methanol to contact the entire internal surface of each container
  - rinsates decanted into polypropylene sample bottles
  - same methanol used for blanks