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, Inc

PFAS Dairy Research

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In collaboration with J.J. Romero, K. Nishimwe, J.B. Poblete, D.Z. Ayala, M.V. Cardoso, A.P. Jimenez

What are PFAS?

- Per-and poly fluoroalkyl substances (PFAS)
- Group of chemicals composed of carbon and fluorine bonds
- Introduced in early 1940's
  - Oil, water and stain repellent properties
  - Heat resistant properties
- Phased out most PFAS in early 2000's

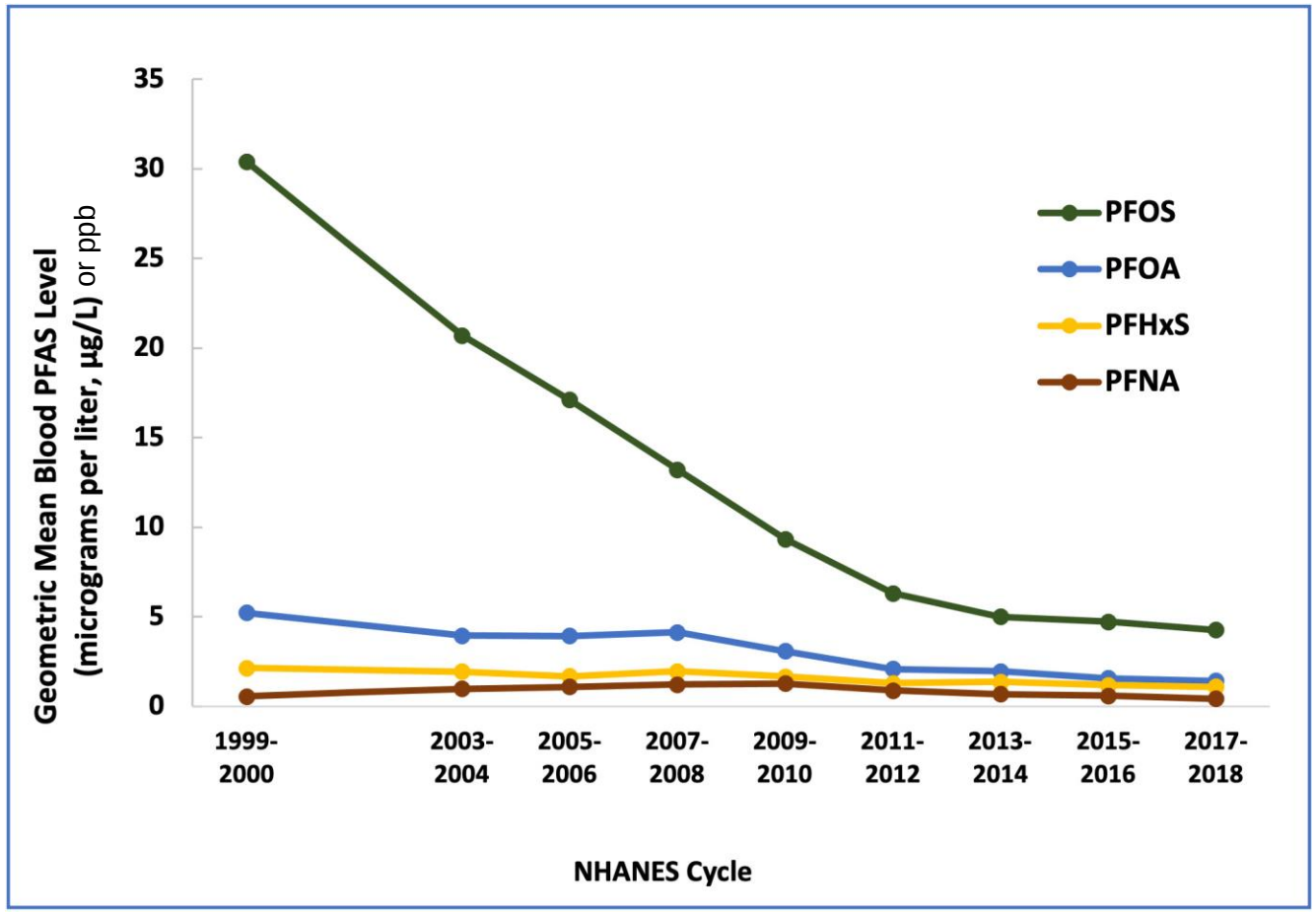
(Ateia et al, 2018; Death et al., 2020; U.S. Agency for Toxic Substances and Disease Registry)

Exposure to PFAS

- Via consumer products, food, water, dust, in utero
  - carpet, fabric, food and packaging, pots and pans, and personal care items.
- Bioaccumulate in the body, liver, kidneys
- Certain PFAS (PFOA and PFOS) linked to health effects
  - cancers, thyroid dysfunction, small reductions in birth weight, and high cholesterol.

(Ateia et al, 2018; Death et al., 2020; U.S. Agency for Toxic Substances and Disease Registry)

Blood levels of the most common PFAS in people in the United States over time



Workers in PFAS manufacturing facilities, communities with contaminated drinking water have higher contamination than general population

From 1999-2000 to 2017-2018, blood PFOA, PFOS declined by more than 70%.

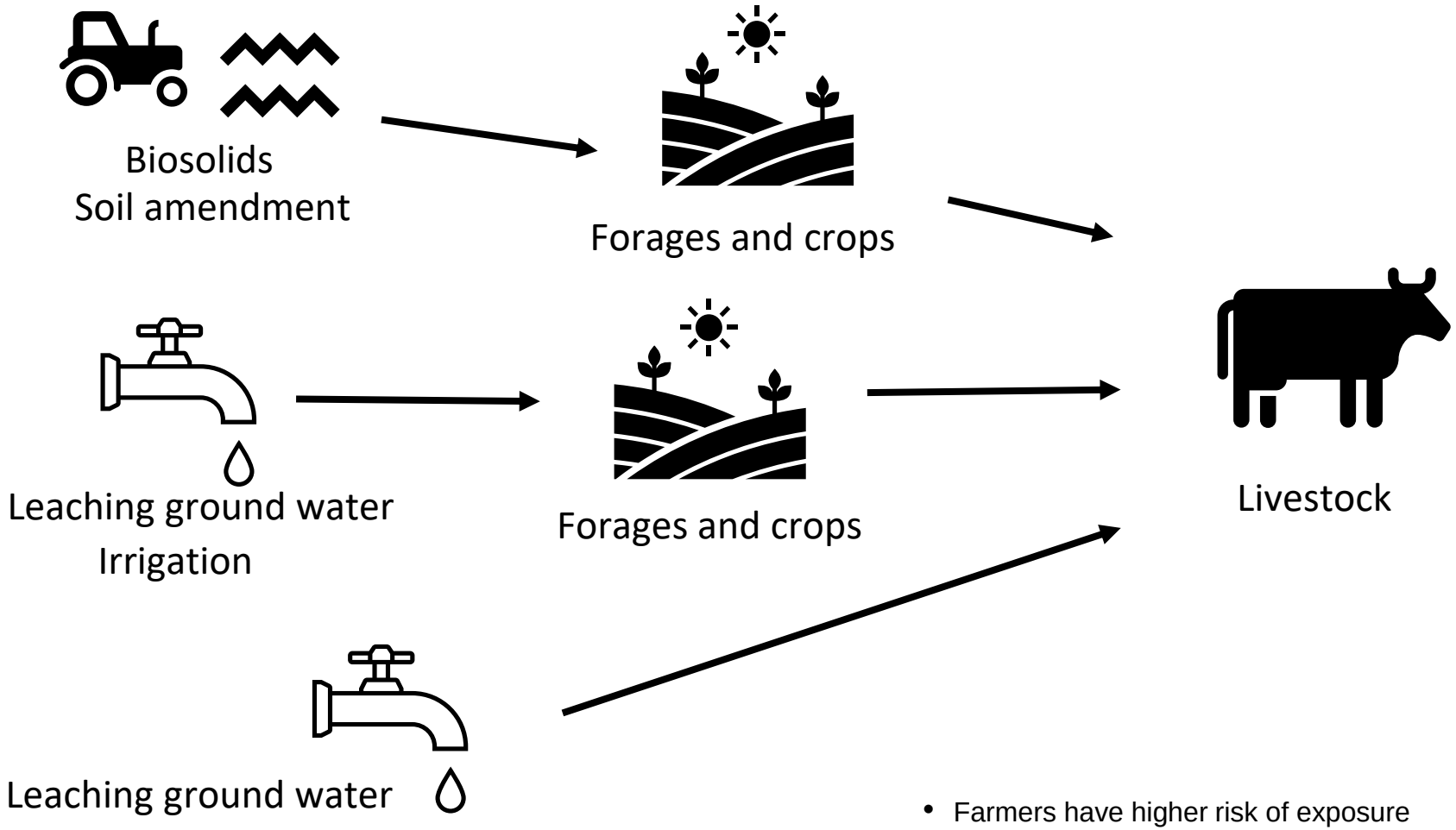
Data Source: CDC. National Report on Human Exposure to Environmental Chemicals, Biomonitoring Data Tables for Environmental Chemicals. https://www.atsdr.cdc.gov/pfas/health-effects/us-population.html

Factors to consider

1. Source of PFAS contamination

    - wastewater sludge and septage, aqueous fire-fighting foam, Department of Defense sites, landfills, water or other.

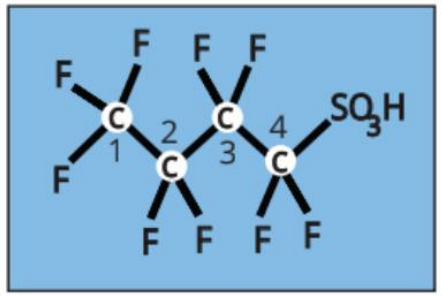
Example of PFAS pathway from the source to farm



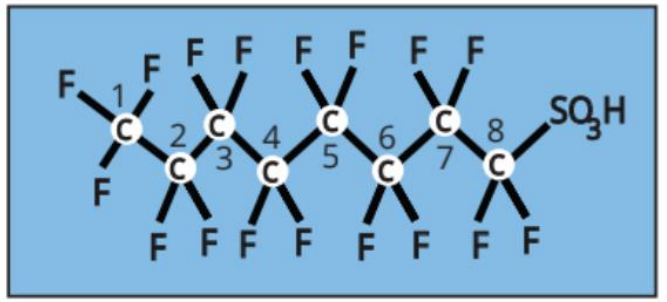
- Farmers have higher risk of exposure
- not all biosolids are contaminated w PFAS

Factors to consider

2. Type of PFAS
   - Carbon length and polar head group



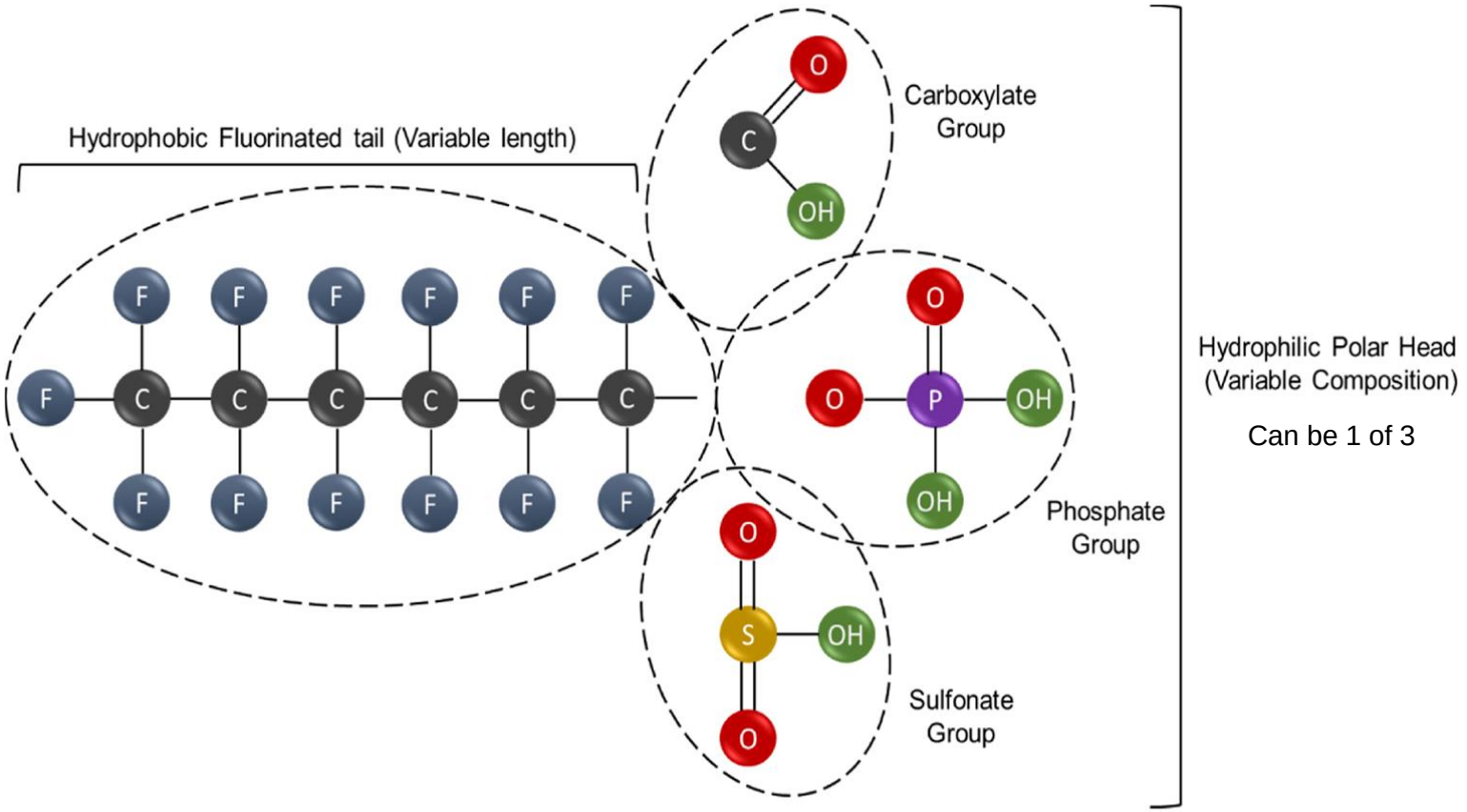
Short chain



Long chain

(where H would be there exists an F)

General structure of non-polymeric, perfluorinated PFAS substances



Tail does not dissolve in water

Head dissolves in water

(Panieri et al. 2022)

Name refers to number of carbons

The total number of carbons used for naming the compound **includes** the carbon in the carboxylic acid functional group (COOH)

Short chain

X	Y	Acronym	Name	Formula
B = buta (4 carbon)	A = carboxylate or carboxylic acid	PFBA	Perfluorobutanoate[1]	$C_3F_7CO_2^-$
			Perfluorobutanoic acid[1]	C_3F_7COOH
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$
			Perfluoropentanoic acid	C_4F_9COOH
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$
			Perfluorohexanoic acid	$C_5F_{11}COOH$
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$

Name refers to number of carbons

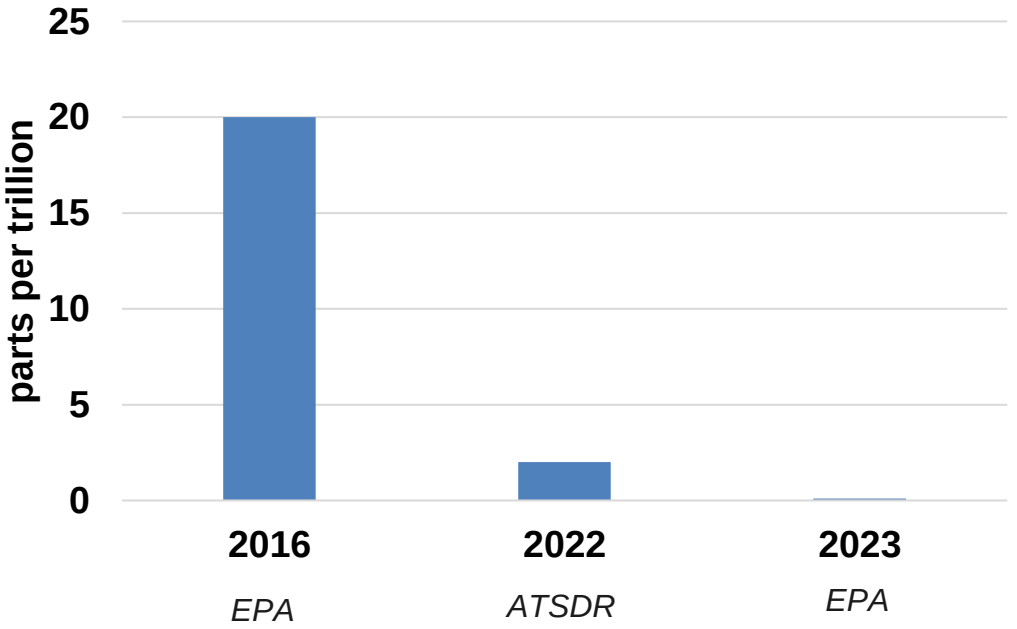
The total number of carbons used for naming the compound **includes** the carbon in the carboxylic acid functional group (COOH)

Long chain

X	Y	Acronym	Name	Formula
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$
			Perfluoroheptanoic acid	$C_6F_{13}COOH$
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$
			Perfluorooctanoic acid	$C_7F_{15}COOH$
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$
			Perfluorononanoic acid	$C_8F_{17}COOH$
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$

Health advisories

U.S. Drinking Water Health Advisories for PFOA and PFOS



individual or combined concentration of PFOA and PFOS.

proposed toxicity values near zero

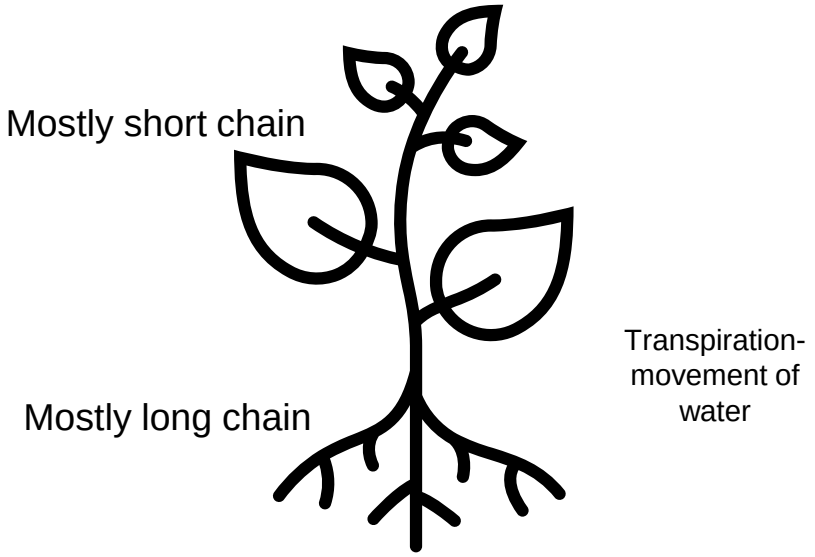
PFAS in Maine

- High PFAS levels reported on agricultural land, water and streams
  - History of biosolid for fertilizer

- Given their persistency, PFAS are mobilized from the soil, through the root system and into the stalk and leaves of plants.

PFAS plant uptake

- Root uptake from soil and water
  -irrigation
- Uptake is influenced many factors such as transpiration rate, lipid and protein content, soil OM, pH.
- Preferential accumulation in vegetative structures of plants from greater transpiration stream
  -PFOS transfer into the grain/fruit is minimal
- Need to further understand plant uptake.



-Active/passive uptake of PFAS
-High root protein content supports accumulation

(Sthal et al. 2009, Fischer et al. 2008, Blaine et al. 2013, Ghisi et al. 2019).

Milk and beef have action levels in Maine

Action level- concentration of a chemical in an environmental medium that serves as a threshold to determine if further action is necessary.

Milk[5] (ng/l or ppt)	
Compound	Action Level
PFOS	210

Beef[6] (ng/g or ppb)	
Compound	Action Level
PFOS	3.4

Action levels for PFOS in cow's milk were derived following standard health risk assessment methods.

https://www1.maine.gov/dep/spills/topics/pfas/Maine-PFAS-Screening-Levels-Rev-6.28.21.pdf

How are action levels determined?

$$\text{Action level} = \frac{\text{Toxicity value}}{\text{Consumption rate}}$$

*toxicity value represents an estimate of an oral daily dose of a chemical below which there is likely to be minimal risk of any deleterious health effects

- Maine CDC developed the PFOS milk action level.
- EPA reference dose (toxicity value) for PFOS in water of 20 ng/kg/day, a 90th percentile milk intake level for a 1-2-year-old child.
- Considered background exposure to PFOS from other dietary and environmental sources.

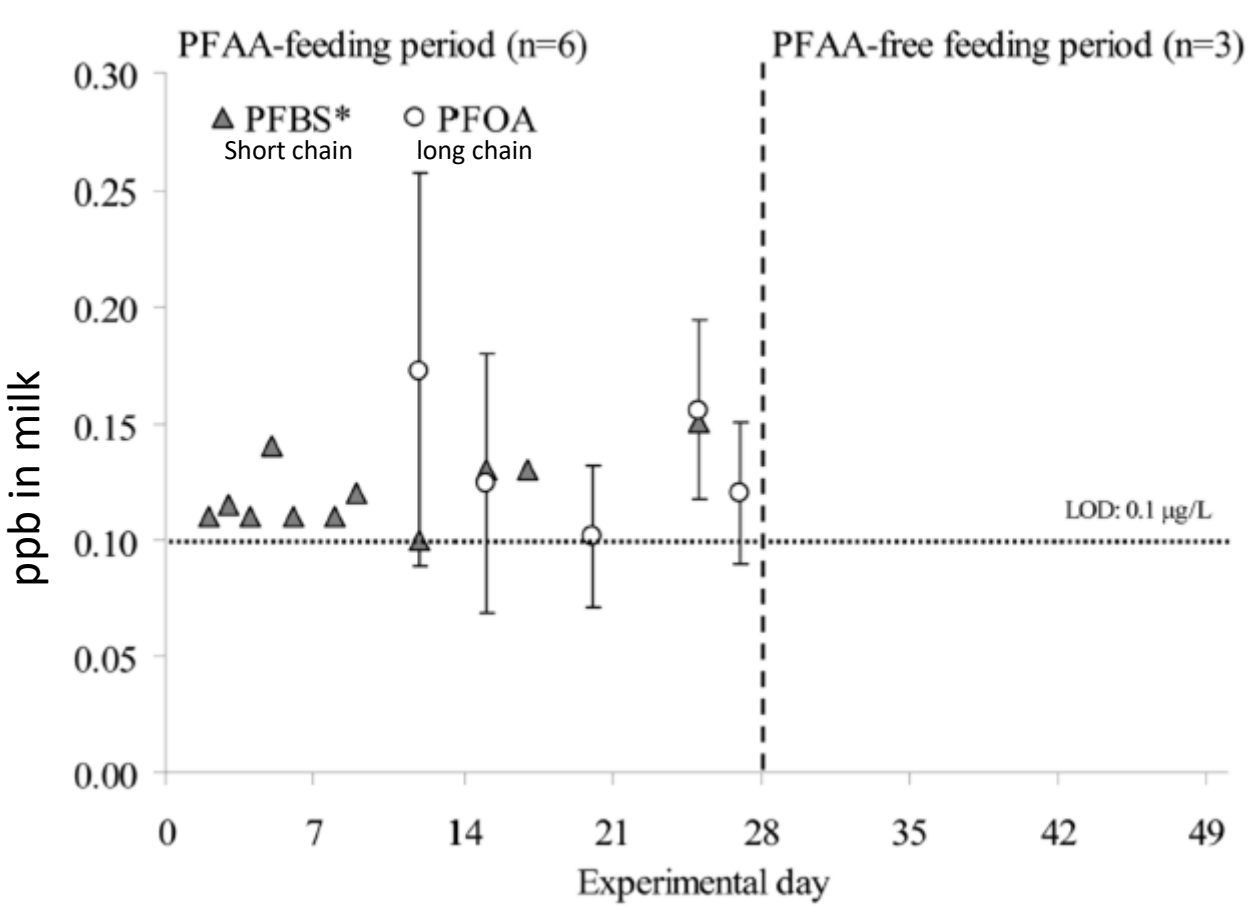
https://www.maine.gov/dep/spills/topics/pfas/Agronomic-Pathway-Soil-Screening-Levels-Soil-Fodder-Cows-Milk-09.16.20.pdf

PFOS and Cattle

THE UNIVERSITY OF MAINE

Absorption, Distribution, and Milk Secretion of the Perfluoroalkyl Acids PFBS, PFHxS, PFOS, and PFOA by Dairy Cows Fed Naturally Contaminated Feed

Janine Kowalczyk,*[,†] Susan Ehlers,[§] Anja Oberhausen,[†] Marion Tischer,[†] Peter Fürst,[§] Helmut Schafft,[†] and Monika Lahrssen-Wiederholt[†]



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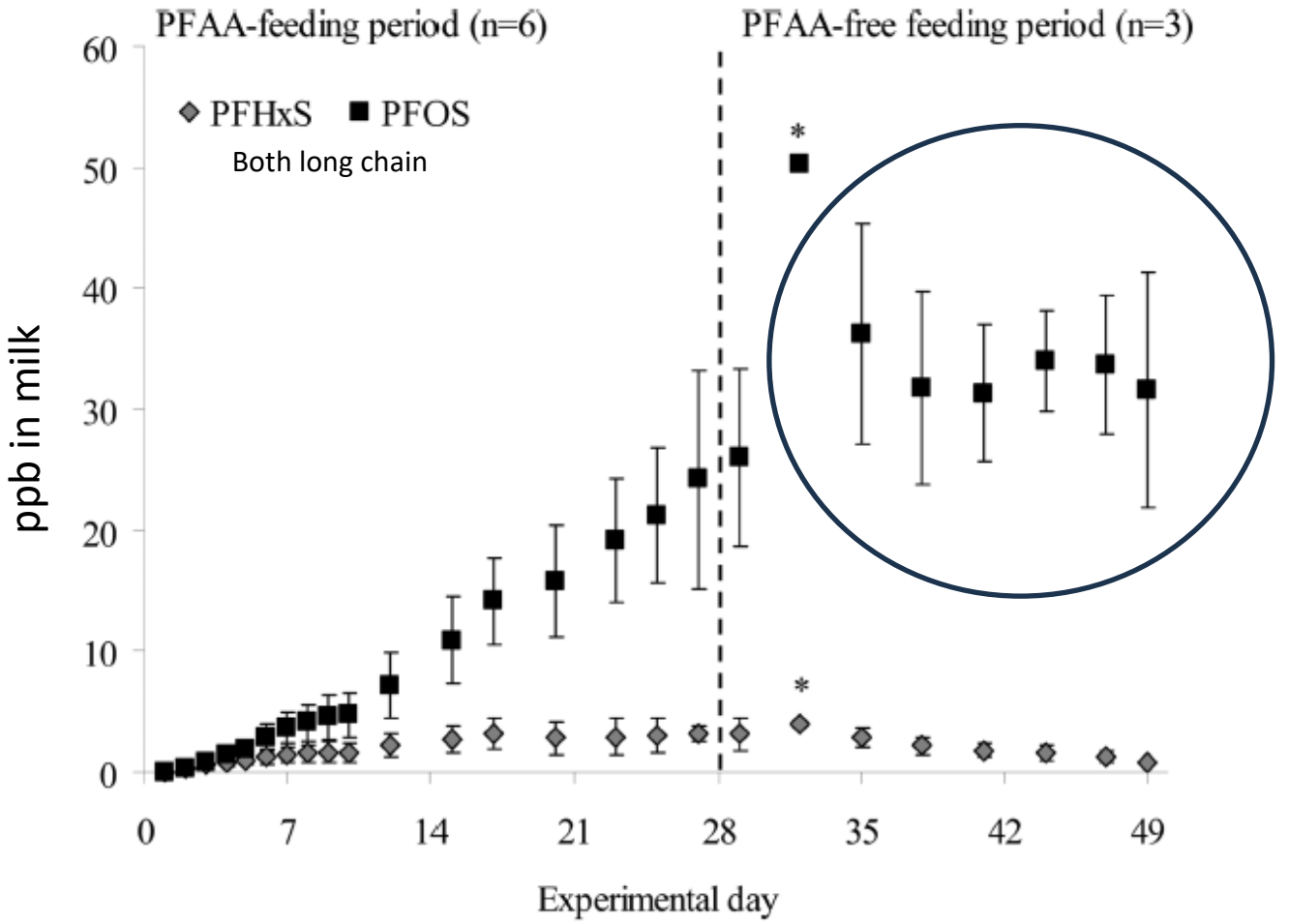
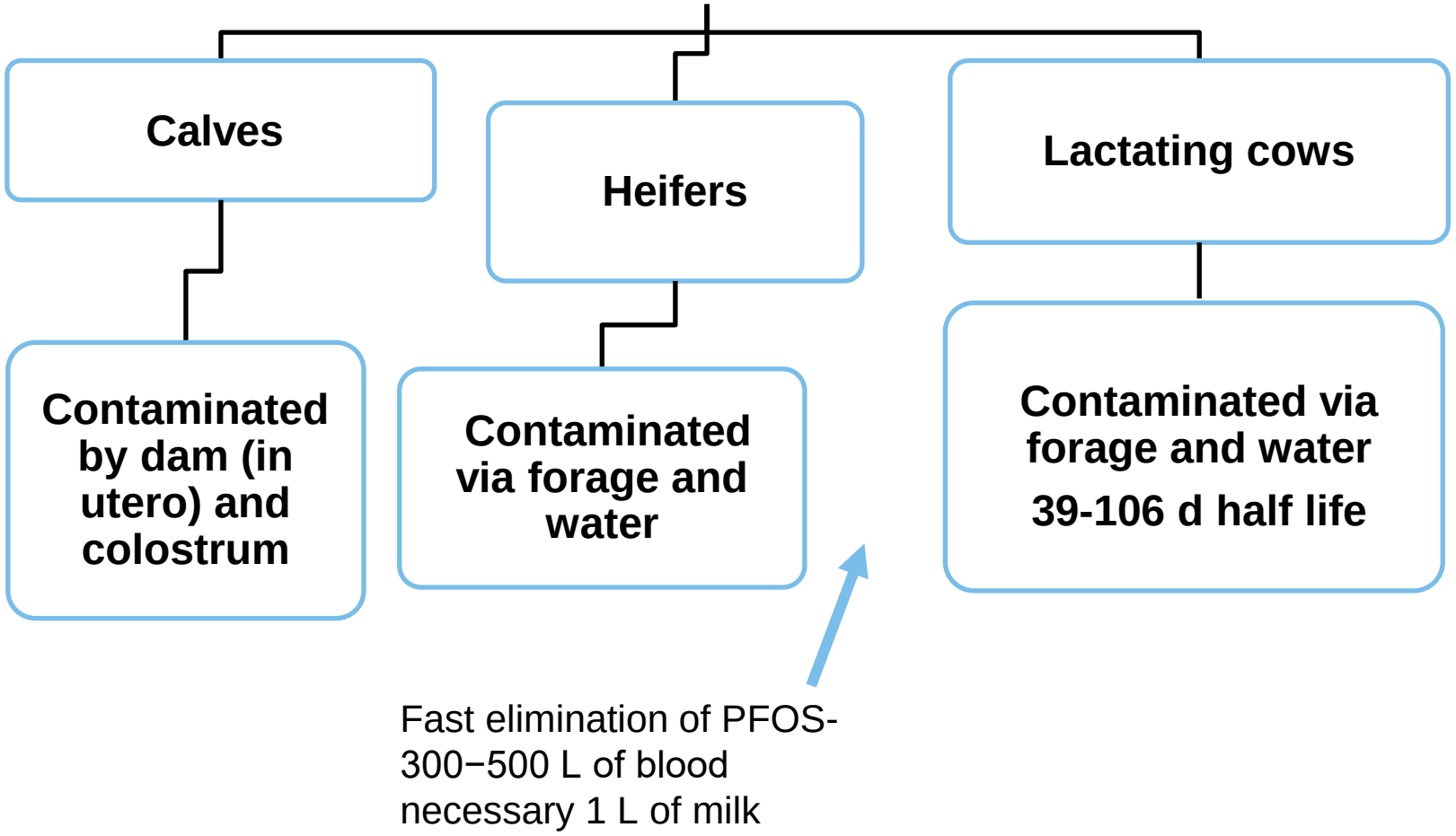


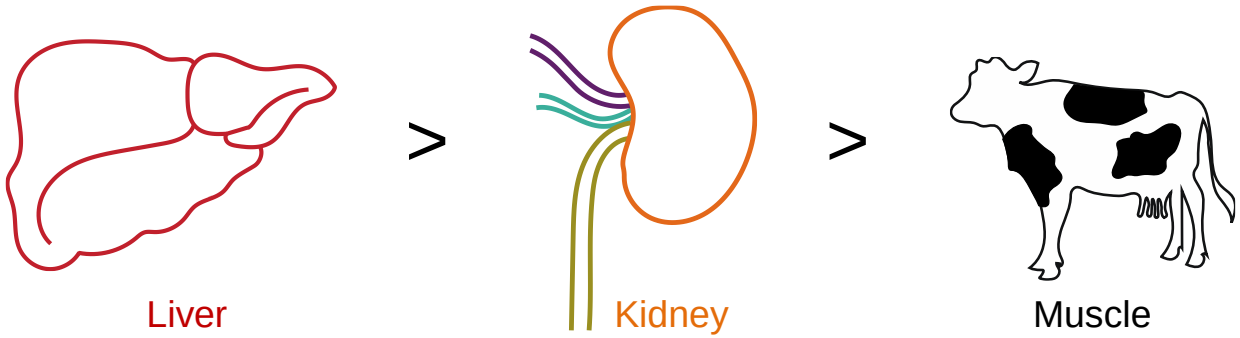
Clean feed eventually leads to reduction in PFAS “half-life”

PFOS ingested and accumulate until secreted in milk



(Kowalczyk et al., 2013; van Asselt, 2013; Death et al., 2020; Lupton et al., 2022)

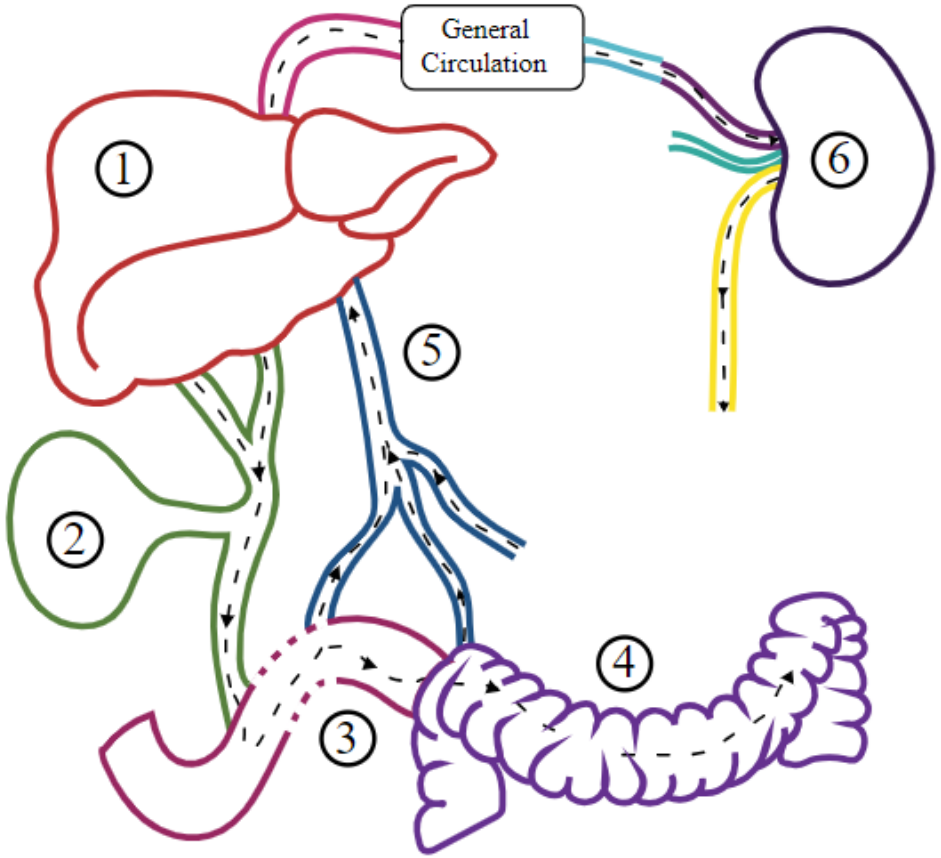
PFOS accumulation in the dairy cow



Muscle has the most mass, but overall concentration is higher in liver

Kowalczyk J., et all., 2013

PFOS bioaccumulate, bind to proteins and are reabsorbed by kidneys

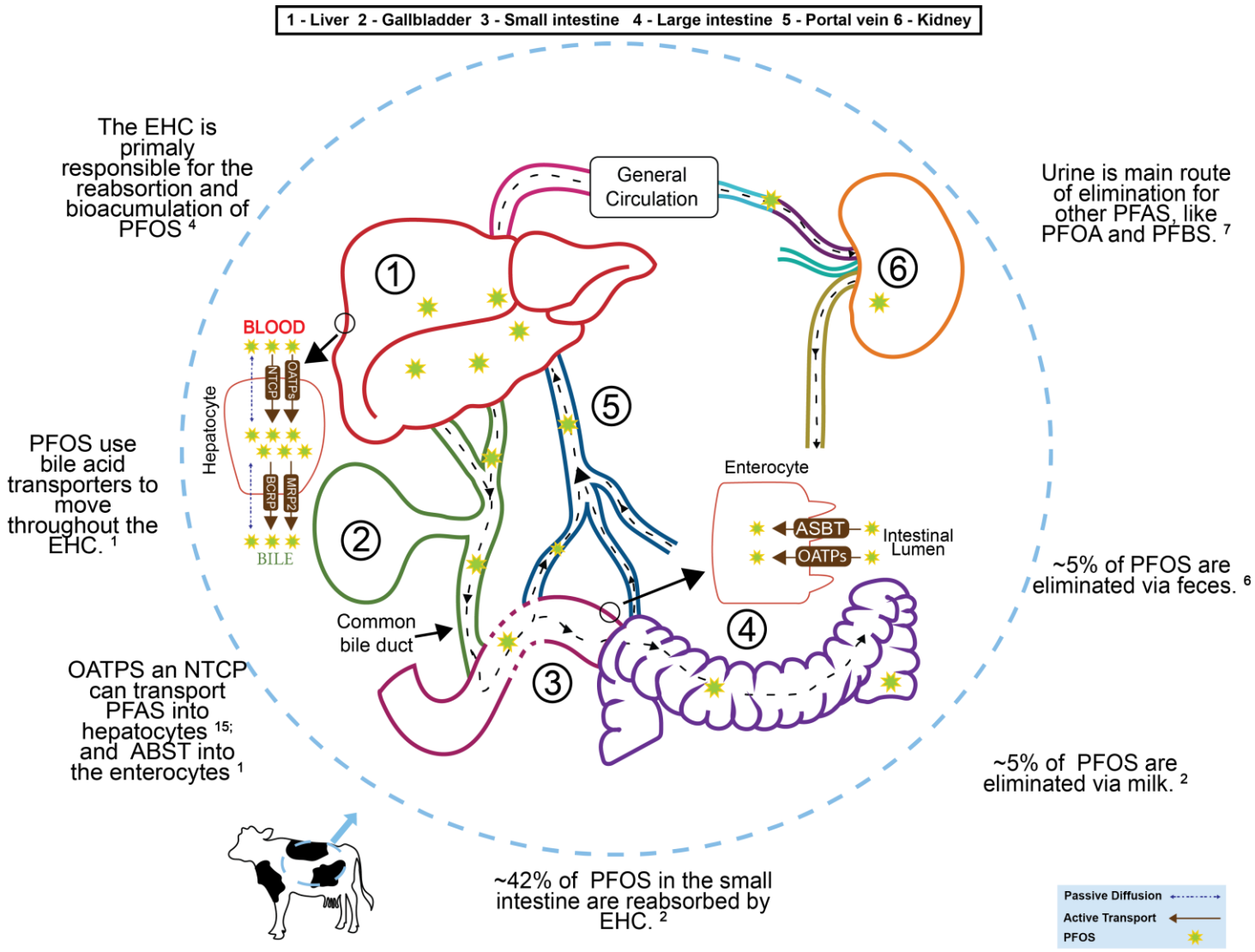


1 - Liver 2 - Gallbladder 3 - Small intestine 4 - Large intestine 5 - Portal vein 6 - Kidney

Bile
-is made and released by the liver, stored in the gallbladder.
-helps with digestion, breaks down fats.

Enterohepatic circulation
-is the movement of bile acids from the liver to the small intestine.

Enterohepatic circulation (EHC) leads to accumulation of PFOS in the liver



OATPS: Organic Anion Transporting Polypeptides / NTCP: Na*/taurocholate cotransportin Polypeptide / ABST: Apical Bile Salt Transport / BSEP : Bile Salt

UMaine PFAS Dairy Team Objectives

Develop educational programs
Conduct applied research

Develop strategies to minimize or lower PFOS in milk

UMaine Current and Future Lines of Research

1. Assess dairy PFAS datasets and trends from dairy farms to generate information to guide decision making/policy, future research, and mitigation strategies.

2. Identify binders and sequestrants that trap and recirculate PFOS.

3. Evaluate pre and post partum feeding management to reduce excretion PFAS during first lactation.

Efficacy of Binders on Per- and Polyfluoroalkyl Substances (PFAS) and Aflatoxin B1 Levels under *In Vitro* Ruminal Conditions

K. Nishimwe[1], **J.B. Poblete[1]**, D.Z. Ayala[1], M.V. Cardoso[1], A.P. Jimenez[1], G. Pereira[2], Y. Jiang[3], and J.J. Romero[1]

[1]Animal and Veterinary Science, University of Maine, Orono ME,
[2]University of Maine Cooperative Extension, Orono ME,
[3]College of Agriculture, Community and the Sciences, Kentucky State University, Frankfort, KY

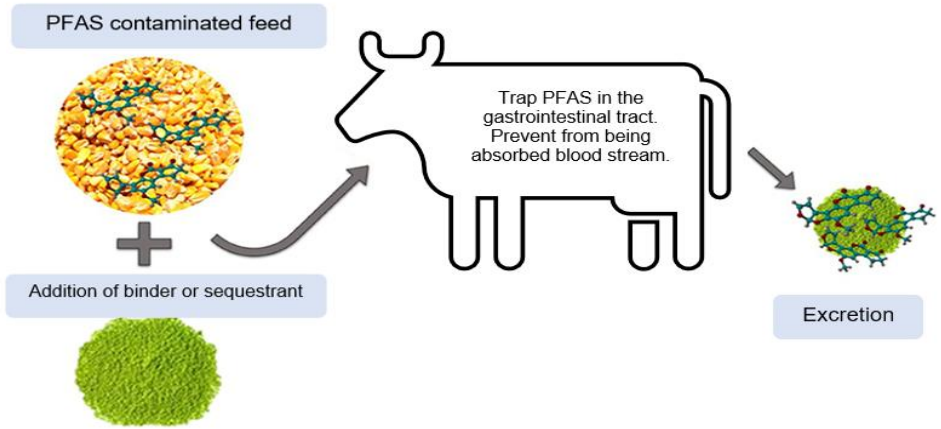
Binder and bile sequestrants have potential to lower PFOS levels

- Binders: material or substance that holds other materials together.
  - Mycotoxin binders used to trap toxins.
    - Aflatoxin B1 (AFB1) is a carcinogenic mycotoxin transferred from contaminated feed to milk.

- Bile sequestrants: disrupt the EHC of bile acids and prevent reabsorption, recirculate via feces.
  - Anion exchange resins increased excretion of PFOS via feces and decreased PFOS in liver. (Johnson et al., 1984)

Objective

Evaluate the efficacy of binders and bile sequestrants in binding PFAS and AFB1 *in vitro*.



Cattle used as filters of PFAS while producing clean milk

Materials and Methods

Aflatoxin B1- positive control of binding

Forage

alfalfa hay
(Medicago sativa)

Treatments

1. Control (CON)
2. Clay binder 1 (CLY-1)
3. (CLY-2)

Materials and Methods

PFOS analysis

Forage

Timothy grass hay*
(*Phleum pratense)* from a
PFAS- contaminated site

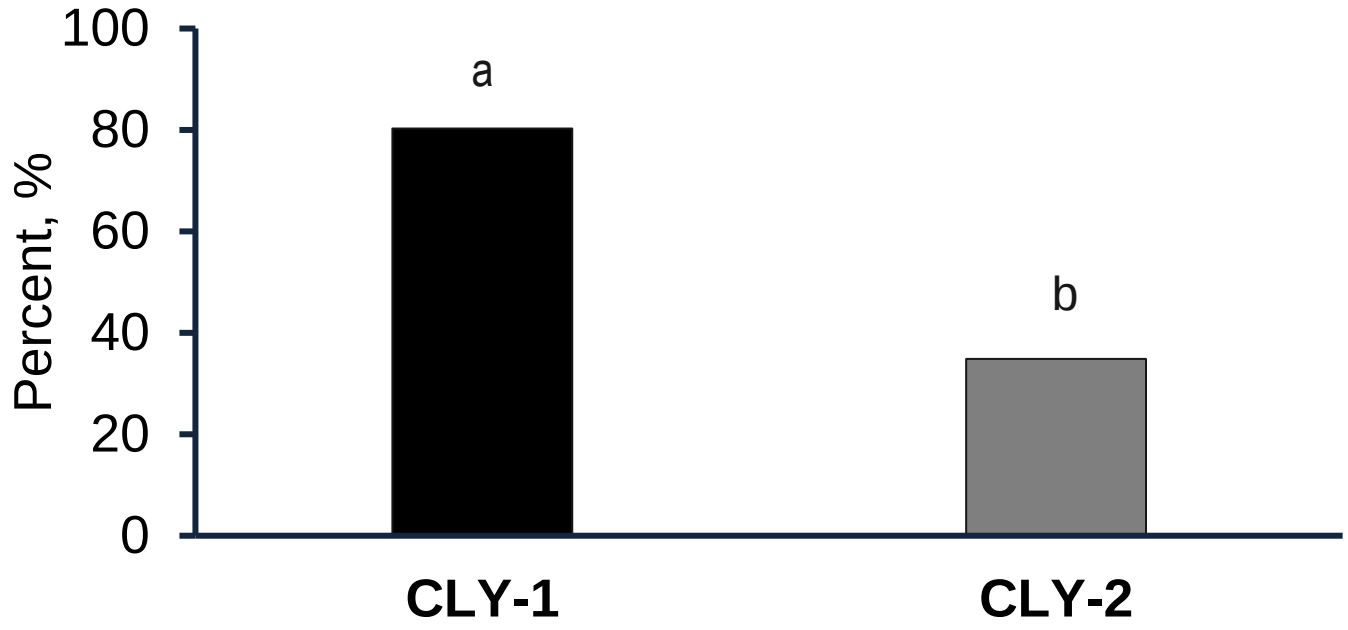
*PFOS: 9.76 µg/kg
PFOA: 1.7 µg/kg
PFHxA: 2.16 µg/kg;
PFPA: 0.6 µg/kg;
PFBS: 0.82 µg/kg; DM basis

Treatments

1. Control (CON)
2. Clay binder 1 (CLY-1)
3. (CLY-2)
4. Polysaccharide binder (PLS)
5. Carbonaceous binder (CRB)
6. Anion Exchange Resin 1 (AER-1)
7. (AER-2)

Bentonite had higher AFB1 binding affinity than montmorillonite clay

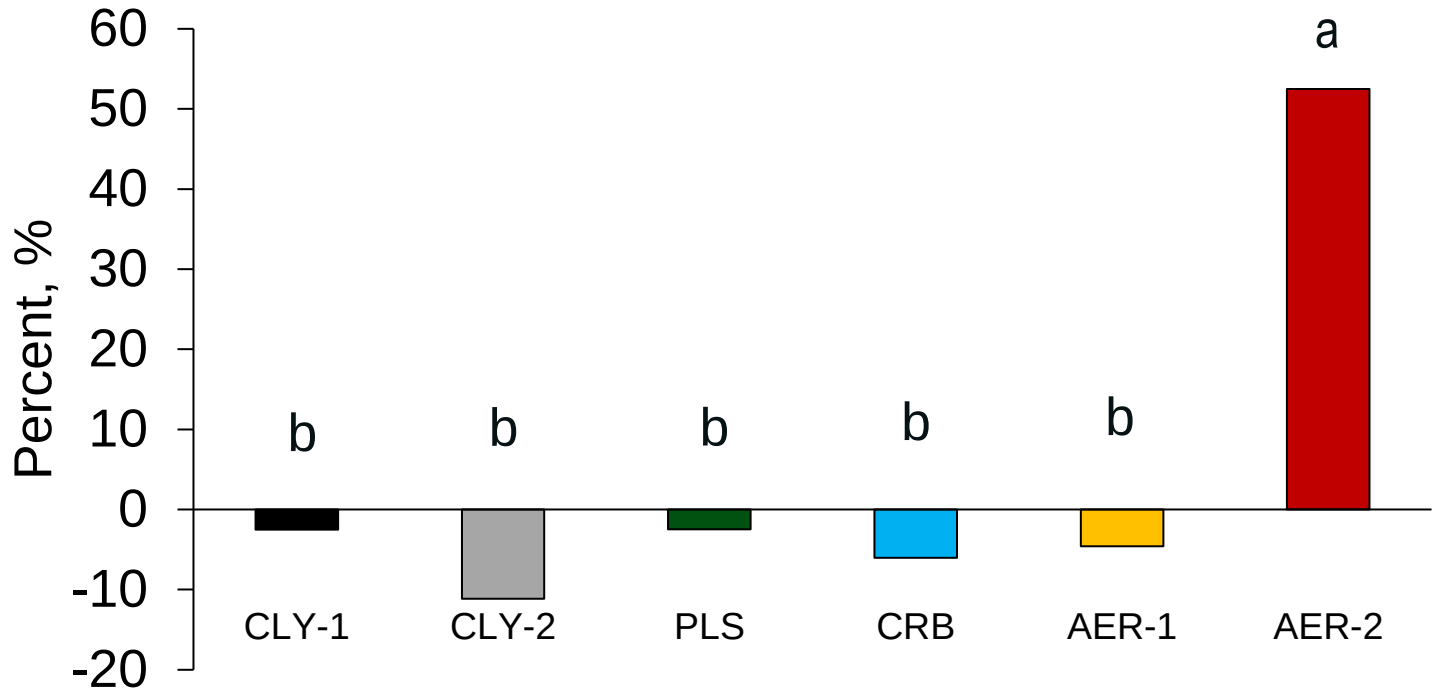
AFB1 binding affinity (%) with binders under *in vitro* ruminal conditions.



SEM=4.84; *P*=0.01.
Note: Means with different superscripts differ significantly (P <0.05)

AER-2 bound 52.46% of PFOS relative to the control

PFOS binding affinity (%) with binders under in vitro ruminal conditions.



SEM=9.83, *P*=0.0009.
Note: Means with different superscripts differ significantly (P <0.05)

Conclusions

- Under in vitro ruminal conditions:
  - CLY-1 exhibited a high ability to adsorb AFB1.
    Confirming the validity of the assay we used.
  - AER-2 demonstrated potential to sequester PFOS.
    The presence of the quaternary ammonium group bound large concentration of PFOS.
- Future research explore the use of resin binders to reduce PFOS contamination.

Steps to Determine PFAS Risk on your Farm

1. Review land application history, nearby sources

2. Identify appropriate steps to conduct sampling
   - water, soil, PFAS free supplies

3. Evaluate lab results
   - PFAS concentrations
     -in soils and solids reported in parts per billion (ppb).
     -in liquids (water and milk) reported in parts per trillion (ppt).

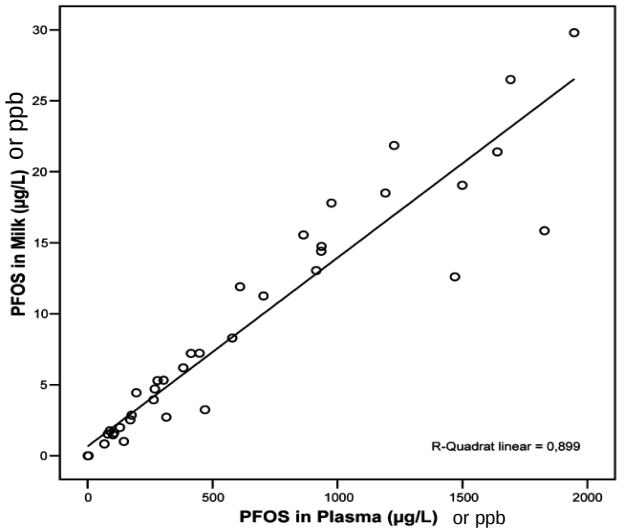
Credit to Rick Kersbergen, UMaine Extension
Visit: https://extension.umaine.edu/agriculture/guide-to-investigating-pfas-risk-on-your-farm/

Methods of detection of PFOS in cattle

- Ear tissue sample testing
- Monitoring blood PFOS levels could determine if cattle are cleared for slaughter (R^2= 0.88; n = 28 cows).
- Monitoring milk PFOS levels could determine blood levels (R^2 = 0.89; n = 6 cows).

Scatter plot for the correlation of PFOS levels in plasma and milk samples during the PFAA-feeding period.

As PFOS concentrations increase less reliable.



Kowalczyk et al., 2013; Johnston et al., 2023

Mitigation options for PFAS contaminated dairy farms

limited by the gaps in current knowledge

1. Explore and implement multiple strategies
   - Binders?
   - Prepartum feeding management
   - Grow lower transport factor crops (hay to corn, or hay to small grains)

2. Implement water filter

3. Feed PFAS clean feed (leads to depuration)

Visit: https://extension.umaine.edu/agriculture/guide-to-investigating-pfas-risk-on-your-farm/

Takeaways

- PFAS is not a Maine only problem
- Livestock and crop farms are not the source of PFAS
- Learn and adapt

Cattle are part of the PFAS solution

Acknowledgements

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Maine Food and Agriculture Center
Maine Department of Agriculture, Conservation, and Forestry

Questions

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