PFAS in the US and Importance in Agriculture

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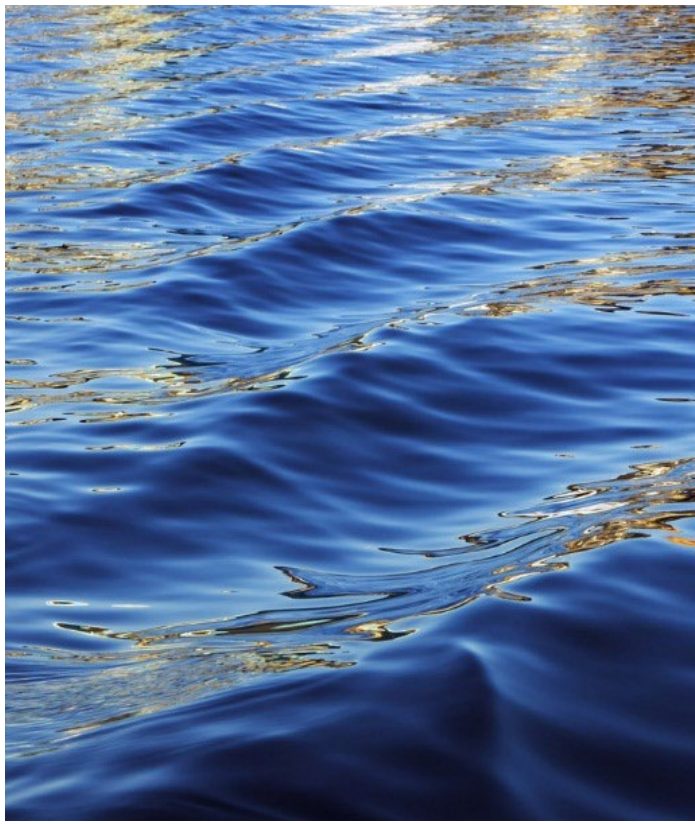
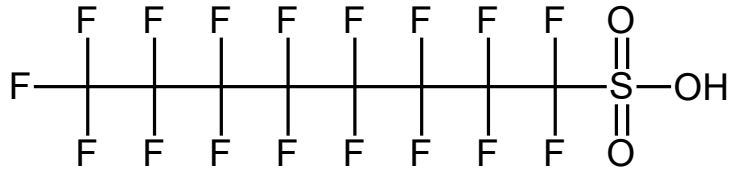


Outline

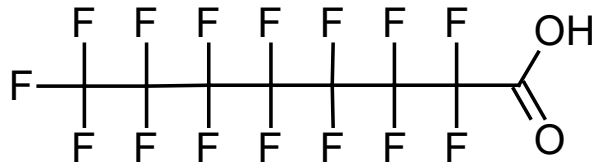
- PFAS Background
- Known and presumptive contamination sites in US
- Why and How affects agriculture
- State PFAS Issues and Efforts
  - Decatur, Alabama
    - Research Project
  - Colorado
  - Maine
  - Michigan
  - New Mexico
    - Research Project
- US Agency Efforts
  - USDA
  - Others

Per- and Polyfluorinated Alkyl Substances PFAS

- Industrially produced chemicals
  - Protective coatings in carpet, apparel and cookware
  - Paper coatings
  - Surfactants
  - Fluoropolymers
  - Aqueous Film-Forming Foam (AFFF)
  - Major products include Teflon® and Scotchgard™
- Why a concern?
  - Persistent and Bioaccumulative
  - Ubiquitous in humans and environment
  - Varying toxicity and effects
    - Immune and liver effects.
  - Multiple routes of exposure
    - Food/diet, dust, air, water

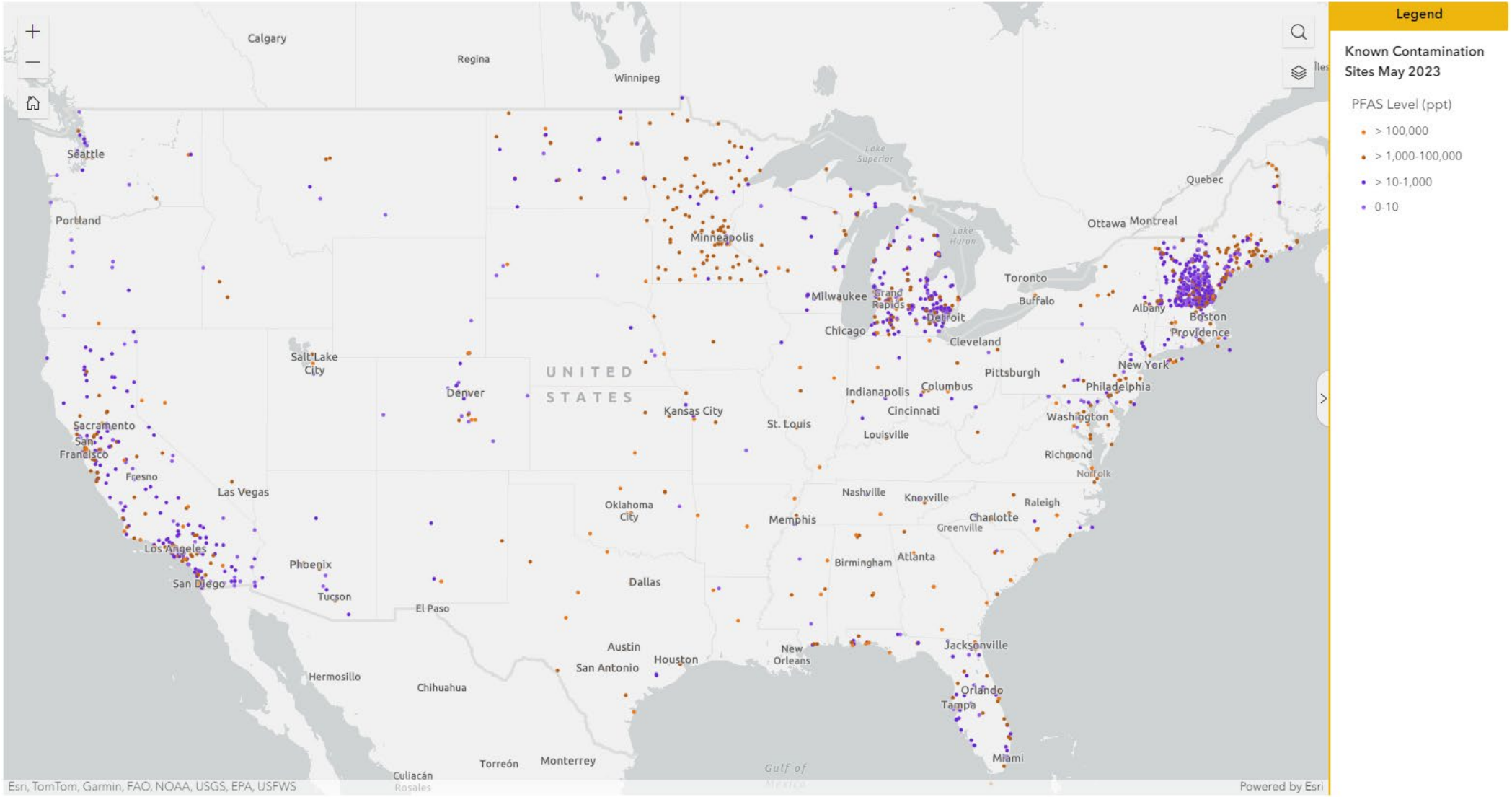


PFOS



PFOA

Known PFAS Contamination Sites



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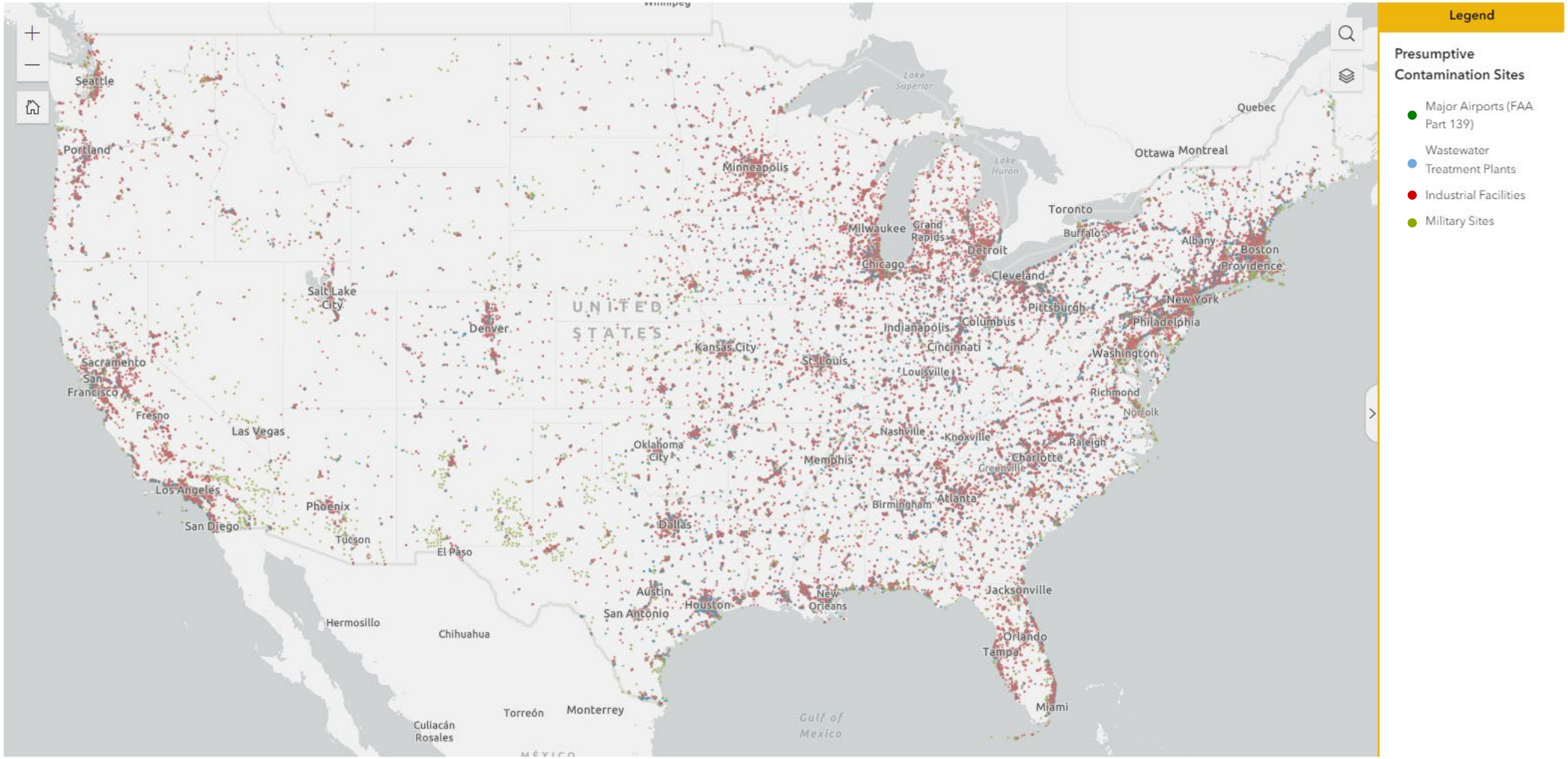
Presumptive PFAS Contamination Sites



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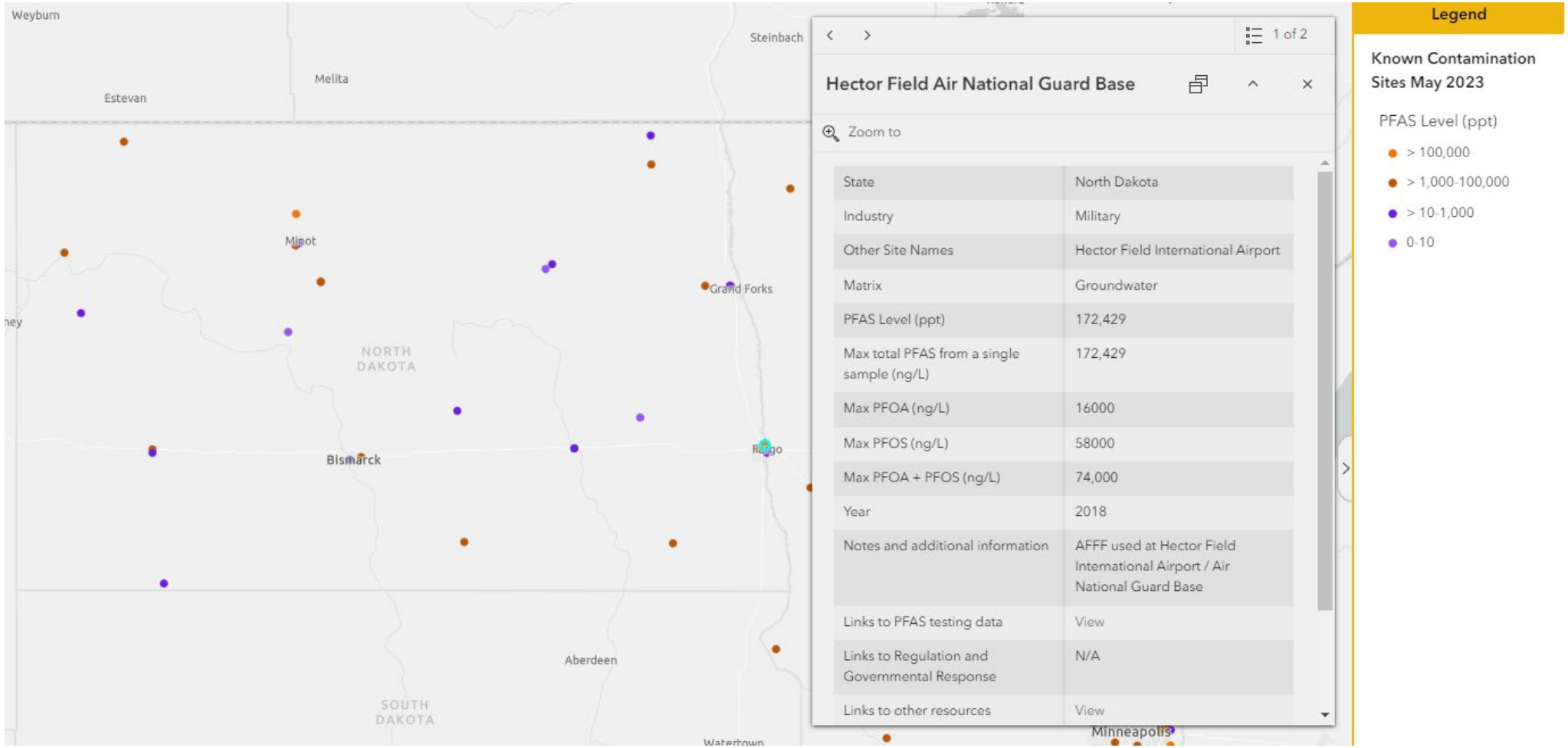
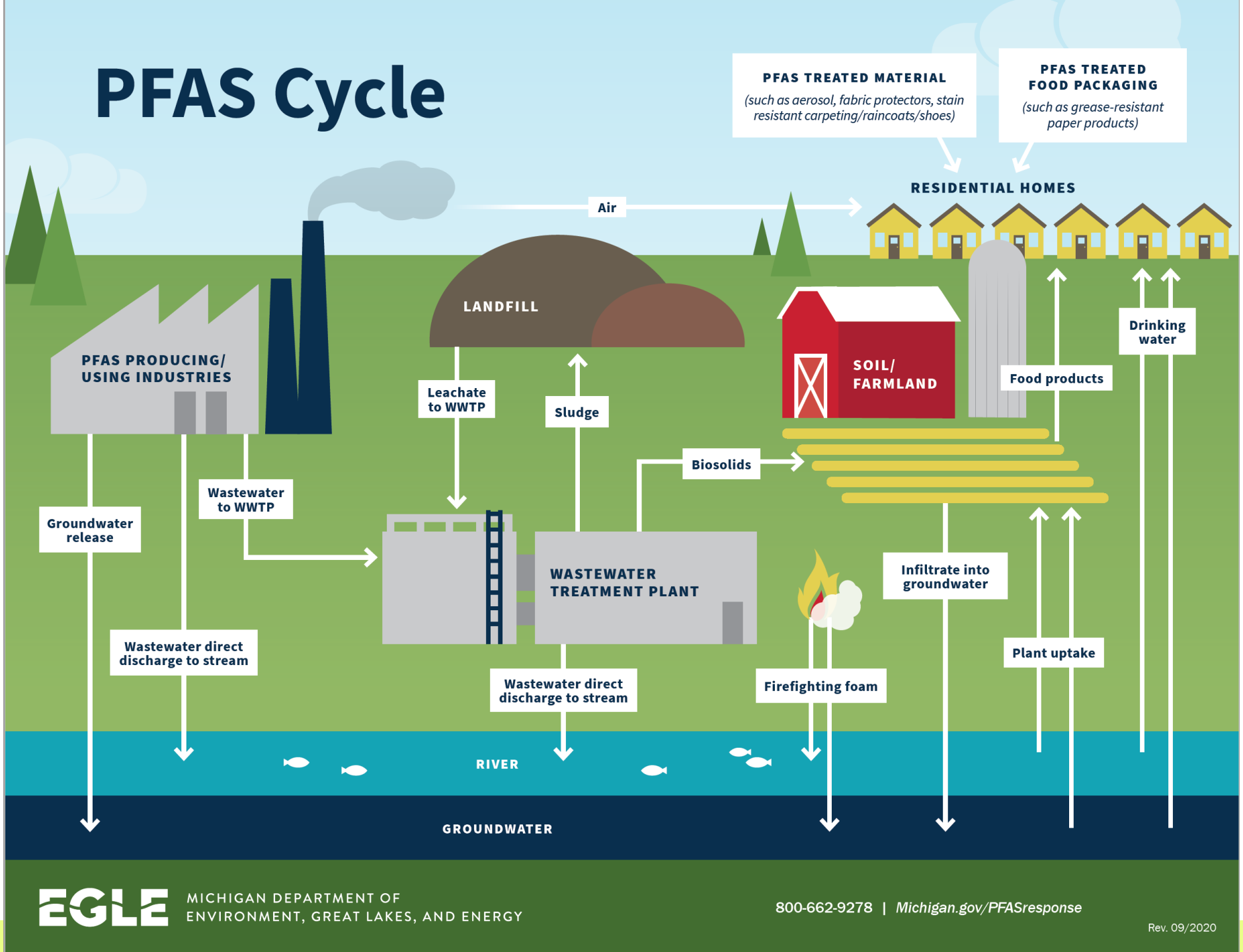
Known ND Contamination Sites



Agricultural PFAS Contamination

- Biosolid application to fields causes soil and water contamination on and near agricultural lands with subsequent crop or feed contamination.
  - Municipal
  - Industrial
  - Paper and textile
- Use of contaminated water (surface or ground) on fields for irrigation.
  - Discharge of PFAS laden wastewater into water ways.
  - Runoff from environmental releases.
    - Biosolid leaching
    - Use of AFFF for firefighting or trainings
- Livestock can be exposed through water and feed sources
  - Feed Contamination
  - Use of contaminated surface and ground water for watering livestock

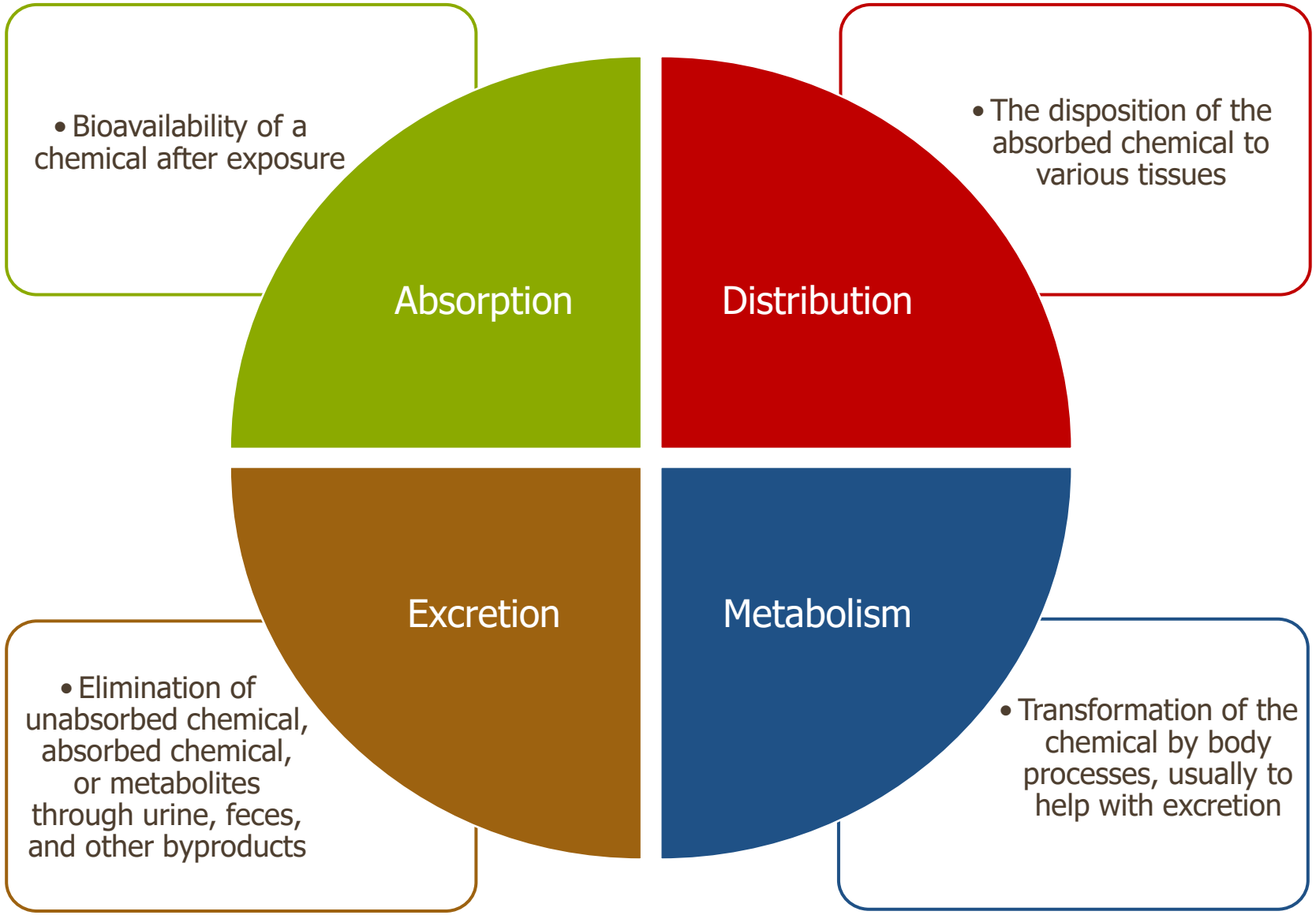

PFAS Cycle
PFAS TREATED MATERIAL
(such as aerosol, fabric protectors, stain resistant carpeting/raincoats/shoes)
PFAS TREATED FOOD PACKAGING
(such as grease-resistant paper products)
RESIDENTIAL HOMES
Air
LANDFILL
PFAS PRODUCING/ USING INDUSTRIES
SOIL/ FARMLAND
Drinking water
Food products
Leachate to WWTP
Sludge
Biosolids
Groundwater release
Wastewater to WWTP
WASTEWATER TREATMENT PLANT
Infiltrate into groundwater
Wastewater direct discharge to stream
Wastewater direct discharge to stream
Firefighting foam
Plant uptake
RIVER
GROUNDWATER
EGLE
MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY
800-662-9278 | Michigan.gov/PFASresponse
Rev. 09/2020

Decatur, Alabama
PFAS

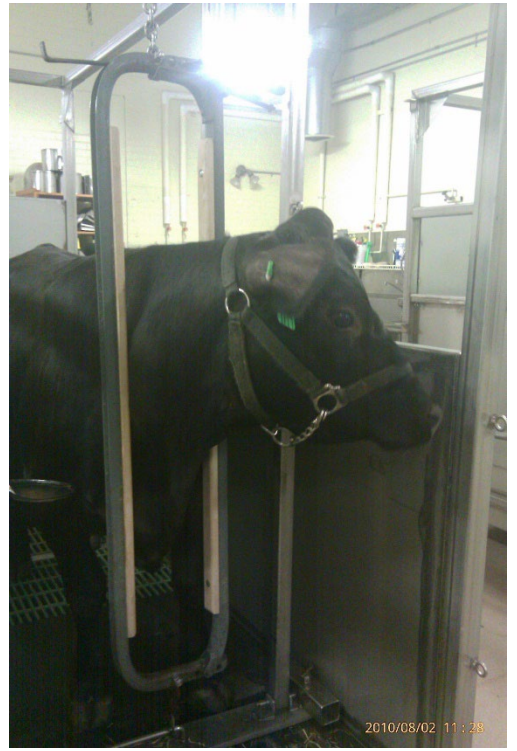
- In 2008, US EPA discovered some of the highest PFOS and PFOA concentrations along with other carboxylic acids and fluorotelomer alcohols in U.S. soils analyzed to that date.
  - Levels in soil of PFOS and PFOA were in the low part per million.
  - Traced back to treated municipal sewage sludge or biosolids contaminated with industrial waste from a perfluoro chemical plant.
  - Biosolids/sludge had been applied to grasslands used for grazing beef cattle.
  - One of the first incidents to determine if biosolid application could be traced to contaminated meat.

- In 2009, US EPA tested wells and ponds in the area surrounding fields spread with biosolids and found that 25% of the samples exceeded the then short-term provisional health advisory limit of 0.4 ug/L or 400 ng/L (ppt) for PFOA. All PFOS concentrations were below the 0.2 ug/L or 200 ng/L public health advisory limit at the time.
- As a result of this testing USDA Food Safety and Inspection Service decided to do additional research on the accumulation of PFOA and PFOS in beef cattle to determine if there was any risk to consumers.

ADME


• Bioavailability of a chemical after exposure
Absorption
Distribution
• The disposition of the absorbed chemical to various tissues
Excretion
Metabolism
• Elimination of unabsorbed chemical, absorbed chemical, or metabolites through urine, feces, and other byproducts
• Transformation of the chemical by body processes, usually to help with excretion

PFOA and PFOS 28-Day Study: PFOA Summary



- PFOA
  - Approximately 100% of PFOA was absorbed and excreted in urine within the first week after dose. Minimal amounts of PFOA were excreted in feces.
    - Due to rapid and complete excretion of PFOA in urine, concentrations in tissues were undetectable.
    - **Data indicated that PFOA might not accumulate in edible tissues of beef cattle**.

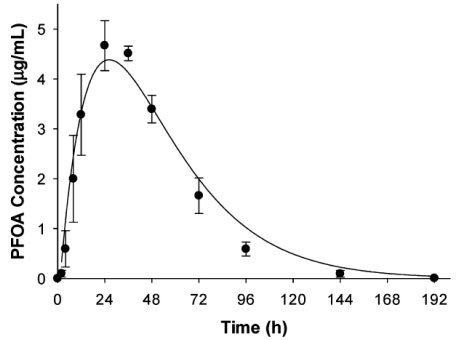


Figure 1. Plasma ^{14}C-PFOA concentrations (μg/mL) and time (h) data through 8 days after a single oral dose given to beef steers. Points represent mean concentrations of four animals from LSC analysis ± one standard deviation. The curve was predicted using a two-phase noncompartmental method.

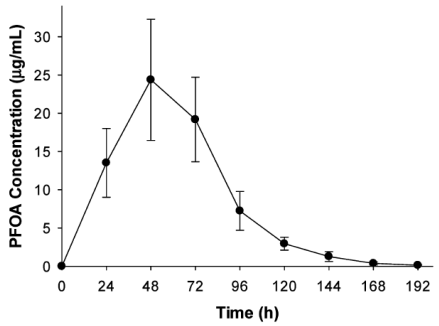


Figure 2. Urine ^{14}C-PFOA concentrations (μg/mL, mean ± SD) and time (h) data through 9 days after a single oral dose given to beef steers. Points represent mean concentrations for four animals from LSC analysis ± one standard deviation.

	urine		
time (days)	total mass (mg)	% excreted	cumulative total %
1	77.4 ± 9.9	21.8 ± 2.8	21.8
2	132.9 ± 14.1	37.5 ± 4.0	59.4
3	86.1 ± 5.7	24.3 ± 1.6	83.7
4	35.9 ± 7.3	10.1 ± 2.0	93.8
5	16.9 ± 2.0	4.8 ± 0.6	98.6
6	4.5 ± 1.5	1.3 ± 0.4	99.9
7	2.0 ± 0.6	0.55 ± 0.2	100.6
8	0.60 ± 0.2	0.17 ± 0.06	100.7
9	0.34 ± 0.1	0.097 ± 0.04	100.7
10–28	<LOQ		

PFOA and PFOS 28-Day Study: PFOS Summary

- PFOS
  - Not significantly excreted in urine and approximately 17% was excreted in feces.
  - PFOS levels remained elevated in plasma and ~**36% of the dose was still circulating in the animal body**.
  - Liver had the highest PFOS tissue concentration.
  - Based on excretion data, it would take ~116 days for half of the PFOS dose to be eliminated **indicating possible accumulation could occur in edible tissues of beef cattle after long term exposure.**

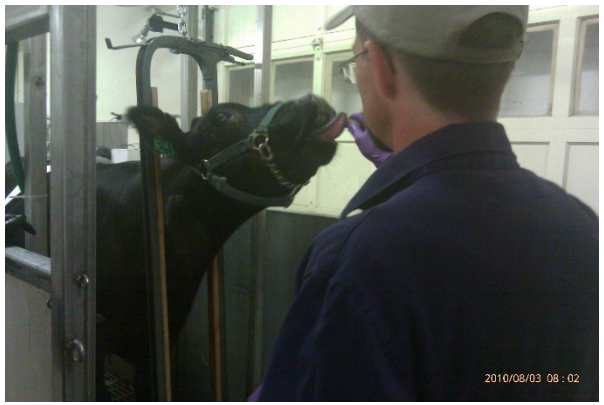


Table 1. Mass Balance Mean (n = 3) Amounts and Percentages for PFOS in Steer Body Compartments at 28 Days Following Dosing

tissue	total amount[a] (mg)	% of dose
plasma	946.7 ± 113.2#	35.8 ± 4.3
feces (0–28 days)	291.1 ± 34.0*	11.0 ± 1.3
carcass remainder	149.6 ± 41.8#	5.7 ± 1.6
muscle	113.8 ± 15.9#	4.3 ± 0.6
liver	58.8 ± 5.5#	2.2 ± 0.2
bile	24.1 ± 13.6#	0.9 ± 0.5
urine (0–28 days)	14.5 ± 1.9*	0.5 ± 0.07
lung	12.8 ± 11.8#	0.5 ± 0.4
kidney	3.1 ± 0.9#	0.1 ± 0.03
spleen	1.4 ± 0.3#	0.05 ± 0.01

[a](*) Total sum for all days of study. (#) Total from slaughter.

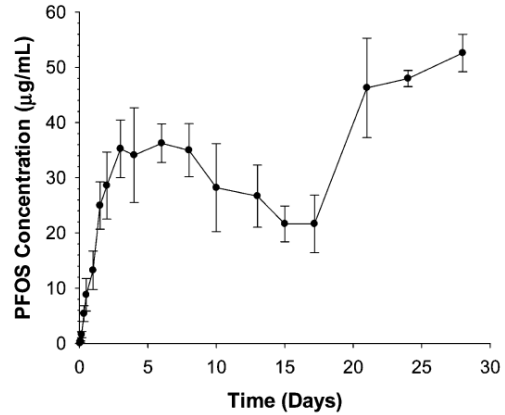


Figure 1. Mean plasma PFOS concentrations (μg/mL) and time data through 28 days after a single oral dose given to steers. Points represent mean concentrations of three animals from LC–MS/MS analysis ± one standard deviation.

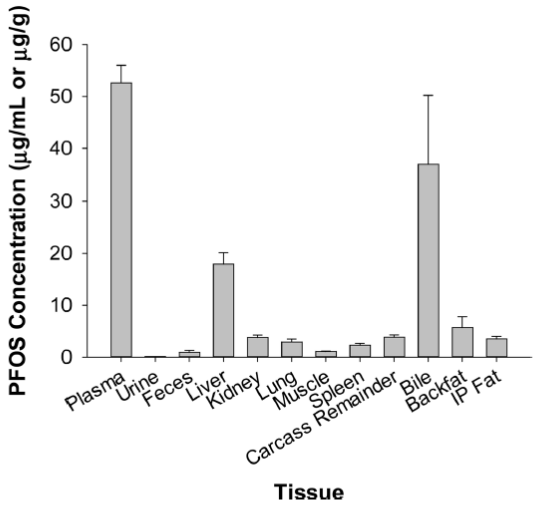


Figure 4. Mean tissue PFOS concentrations (μg/mL or μg/g) after 28 days following a single oral dose given to steers. Columns represent mean concentrations of three animals from LC–MS/MS analysis ± one standard deviation. Day 28 plasma, urine, and fecal concentrations are shown for comparison.

PFOS Half-Life Study: Summary

- Whole body (28-day steers) and plasma (heifers and steers, half-life study) PFOS half-lives were not significantly different between the short and long studies.
- Except for plasma, liver continued to have highest PFOS tissue concentration, followed by kidney.
- **<u>Muscle had some of the lowest tissue concentrations</u>**.
- PFOS tissue depletion half-lives ranged from 36 days in backfat up to 385 days in kidney.
  - Liver half-life was comparable to those observed in the whole body and plasma at 116 days.
  - Muscle half-life was longer at 165 days, indicating that even a single exposure will take time to clear from an animal and chronic exposure could be even longer.

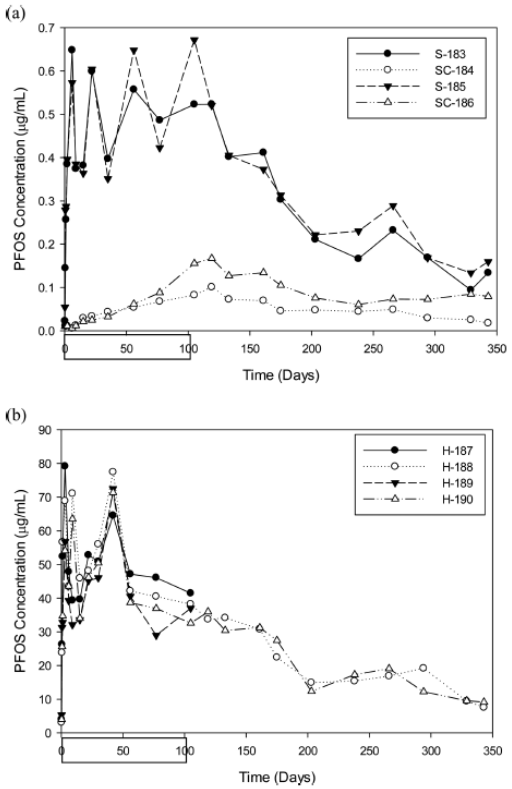


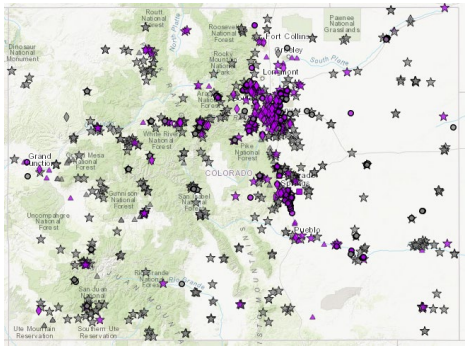
Figure 1. Plasma PFOS concentrations in individual steers (a) and heifers (b). SC stands for steer control; S stands for steer; and H stands for heifer. Box around 1−111 days is time animals were in pasture.

Table 1. Average PFOS Tissue Concentrations (µg/g ww) with Standard Deviations for Low-Dose Steers (0.098 mg/kg bw) and High-Dose Heifers (9.1 mg/kg bw)

tissue	steers[a]	heifers (105 days)[b]	heifers (343 days)[c]
liver	0.149 ± 0.015[d]	8.76 ± 3.54	4.74 ± 0.56[d]
kidney	0.082 ± 0.024[d]	3.96 ± 0.16	2.36 ± 0.57[e]
back fat	0.037 ± 0.009[f]	1.26 ± 0.14	0.87 ± 0.11[f]
IP fat	0.014 ± 0.002	0.93 ± 0.08	0.33 ± 0.05
skin	0.008 ± 0.010	NC[g]	0.69 ± 0.86
shoulder	0.004 ± 0.001	1.20 ± 0.46	0.27 ± 0.01
tenderloin	0.007 ± 0.001	0.36 ± 0.04	0.30 ± 0.01
ribeye	0.004 ± 0.000	0.86 ± 0.19	0.17 ± 0.10
rump	0.004 ± 0.001	0.92 ± 0.30	0.39 ± 0.03
bone	0.003 ± 0.001	0.46 ± 0.05	0.23 ± 0.19

[a]Average tissue concentration (n = 2 steers) with low dose of 0.098 mg/kg bw and slaughtered at 343 days. [b]Average tissue concentration (n = 2 heifers) with high dose of 9.1 mg/kg bw and slaughtered at 105 days. [c]Average tissue concentration (n = 2 heifers) with high dose of 9.1 mg/kg bw and slaughtered at 343 days. [d]Significantly different (Bonferroni t test, $p < 0.05$) from all other tissues. [e]Significantly different (Bonferroni t test, $p < 0.05$) from all tissues except skin and back fat. [f]Significantly different (Bonferroni t test, $p < 0.05$) from all muscle cuts and IP fat. [g]Not collected.

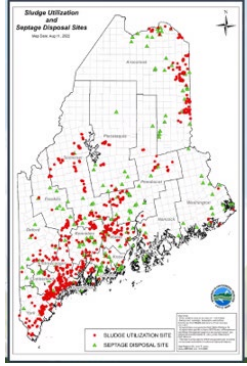
Colorado PFAS Contamination



- In 2016, a PFAS contamination plume was discovered by the US EPA in the aquifer that serves several municipalities and rural areas including farms.
- PFAS contamination came from Peterson Airforce Base near Colorado Springs, CO and Venetucci Farm.
- PFOA, PFOS, PFHpA, PFBA, and PFHxS were all present in water.
- There was concern that using the water for livestock and irrigation of crops could lead to contamination of meat, milk, eggs, and produce.
- Water levels for PFOA, PFOS, and PFHxS were 0.09 ug/L, 0.1 ug/L and 0.5 ug/L (part per billion). Soil concentrations ranged in the sub-ppb to low ppb range with highest concentrations for PFOS.
- The CO Department of Public Health and Environment led efforts with US EPA, USDA ARS, and Colorado School of Mines to address the problem.
- Since discovery of the PFAS contamination in the aquifer, additional sites of contamination around the state have been discovered including sites with biosolid application.

https://cdphe.colorado.gov/water-Biosolids-PFAS

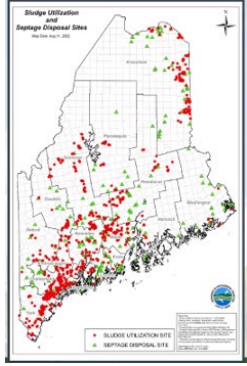
Maine PFAS Contamination



- In 2016, an impacted dairy farm was discovered to have PFAS contamination due to use of contaminated biosolids on fields used to grow animal feed or forage.
  - Resulted in milk PFOS action threshold of 210 parts per trillion (ppt).
- In 2019, Maine governor created the PFAS Task Force to provide recommendations regarding safe drinking water and food, as well as identifying and investigating PFAS in the environment.
- A second dairy in 2020 was identified as contaminated after retail milk testing found 32000 ppt. A third dairy was discovered soon after.
- In the following years (2021-2023), Maine legislature approved PFAS budgets for Departments of Agriculture, Conservation and Forestry (ME DACF), and Environmental Protection (ME DEP) to hire staff and build out technical and financial assistance efforts. A finalized fund of $60 million was approved in 2023. Additional assistance for PFAS testing has also been provided by ME Center for Disease and Prevention.
- Maine has discovered 70+ farms with varying levels of contamination and varying farming practices.
  - Contaminated products include milk, beef, pork, produce, fodder and byproducts such as manure and compost.
  - Health concerns for farmers and families has also been raised.

https://www.maine.gov/dacf/ag/pfas/index.shtml
https://www.maine.gov/dep/spills/topics/pfas/#Timeline

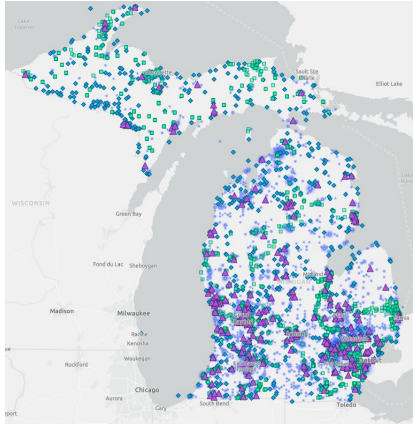
Maine PFAS Contamination



- Maine has established an interim drinking water standard set in 2021 of 20 ppt for the sum of 6 PFAS.
- Additional testing of >1000 licensed septage and sludge land application sites is required to be completed by 2025 (1750 private well samples, 400+ soil samples).
- Maine has set Action Thresholds for PFOS in milk (210 ppt) and beef muscle (3.4 ppb) as well as soil screening levels to determine risk of crop uptake for dairy farms which are feed crop specific. Additional action thresholds are being developed in other animal products. Levels are updated as new information and research is released.
- Maine has also established a working relationship with outside agricultural organizations such as Maine Farmland Trust to provide more rapid assistance (PFAS Emergency Relief Fund) to farmers impacted by contamination.
- Maine is also supporting PFAS research and establishing a Research Farm from one of the contaminated farms.
- Maine has also discovered increased levels of PFAS in deer, wild turkeys, and fish. An action level at 3.5 ppb in fish has been established.
- Maine has currently banned the spreading of biosolids on agricultural fields.

https://www.maine.gov/dacf/ag/pfas/index.shtml
https://www.maine.gov/dep/spills/topics/pfas/#Timeline

Michigan PFAS Contamination



- In 2017 the Michigan PFAS Action Response Team (MPART) was established and consists of 7 state agencies to ensure coordination in implementing a response to PFAS contamination in the state.
- In November 2017, the MPART listed 28 sites that included areas of groundwater contamination as well as rivers and public water systems for investigation. In 2018 the site definition changed where one or more monitoring results exceeds groundwater clean-up criteria at 70 ppt of PFOS and PFOA individually or combined.
- In 2018, MI issues a 'Do Not Eat' advisory for deer taken within 5 miles of Clark's Marsh in Oscoda Township due to high levels of PFAS. In 2019, additional advisories were released for aquatic and semi-aquatic animals near the marsh.
- In 2019 a Century farm in MI was found to have biosolids applied that had industrial waste added to the stream and caused the biosolids to contain over 2000 ppb of PFAS. Monitoring wells were established and in 2021 the beef cattle on the farm were found to be contaminated with meat levels at 1.9 ppb of PFOS.
- In August 2020 the cleanup criteria for groundwater changed to 8 ppt for PFOA and 16 ppt for PFOS.
  - Surface Water Quality values are also established for MI at 170 ppt for PFOA and 12 ppt for PFOS.
- In December 2020 an additional 5 PFAS compounds were added to the list.
- In 2021, MI set a biosolid standard of 150 ppb and biosolids must be tested before land application.
- At the end of FY2023, MI has identified a total of 266 PFAS impacted sites based on groundwater criteria.
- Funding has went to the 7 state agencies to continue to support PFAS efforts within the state.
- Continued monitoring of water, biosolids, and wildlife is established.

https://www.michigan.gov/pfasresponse

New Mexico PFAS Contamination

- Fall of 2018 the NM Department of Health (NMDOH) was notified by the NM Environment Department (NMED) about soil and groundwater PFAS contamination at Cannon Airforce Base in Clovis, NM after PFAS monitoring under the Unregulated Contaminants Monitoring Rule discovered PFAS in well water near the Airforce Base.
- Groundwater was contaminated by use of aqueous film-forming foam (AFFF) which is commonly used at military sites and airports for petroleum fire suppression.
- The water contamination resulted in contamination of agricultural fields through irrigation water and a large dairy herd (~5000 head) becoming contaminated through exposure from water and feed.
  - Due to contaminated milk, the dairy could not sell product.
  - Additionally, the level of contamination was a concern and animals were not allowed to go to market.
- In 2019, the NM Department of Agriculture contacted USDA FSIS and ARS to help conduct testing on the herd. Additionally, a study was conducted to see if depuration of the animals was possible.
- Much of the response within state has been by the Department of Agriculture, NMED, and NMDOH, including managing PFAS contaminated carcasses for disposal.
  - Statewide sampling of public water systems and private wells multiple times.
  - Investigation of contamination sources.

https://www.env.nm.gov/pfas/

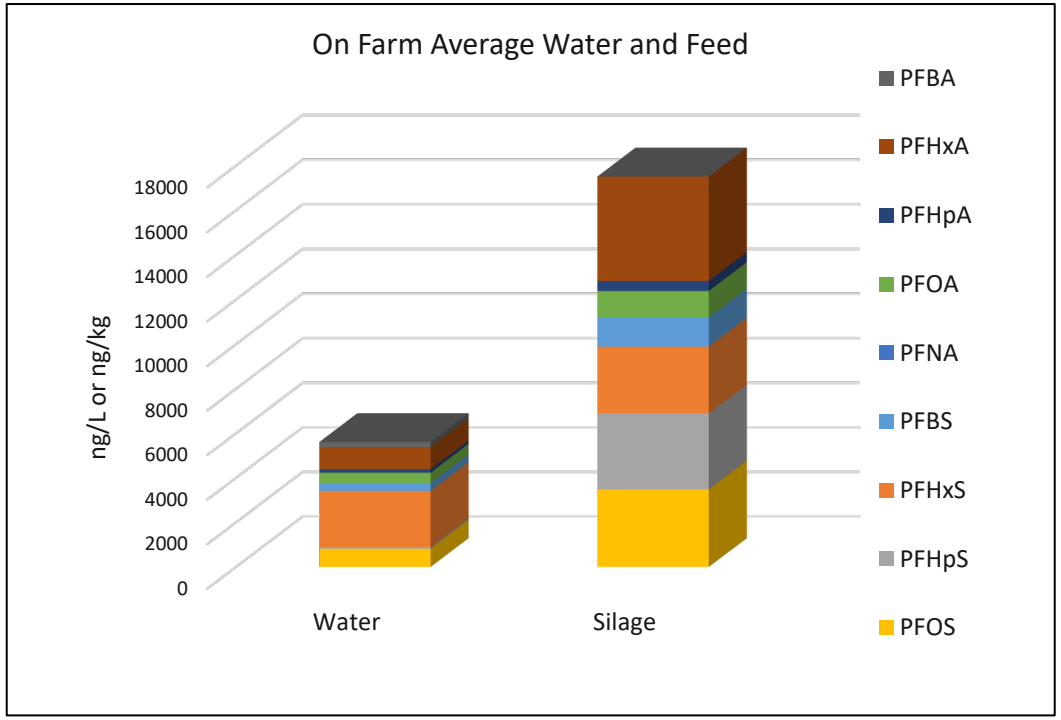
PFAS Work in NM Dairy Cows
On Farm and Depuration Study

- **On Farm sampling** of water, feed, plasma (164 animals; 37 heifers, 97 dry cows, 30 lactating cows) with paired skin ear notch was conducted.
  - **Lupton et al. 2022.** *J. Agric. Food Chem.* **70: 15945-15954.**
- PFAS compounds included 5 carboxylic acids (4-9 carbon) and initially 4 sulfonic acids (4-8 carbon).

- Purchased 10 young heifers, 5 dry cows, and 15 lactating cows from contaminated herd for tissue analysis (5 young, 5 dry, 10 lactating) and depuration study (5 young, 5 lactating)
  - Moved to New Mexico State University, Las Cruces, NM and provided clean water and feed.
  - Tissue collection included muscle, fat, liver, kidney, lung, skin, and fetal tissues from bred dry cows.
  - Histology performed on larger set of tissues.
  - Depuration study, collected plasma, milk, and fecal samples every 2 weeks for PFAS analysis.
    - Necropsy at 2, 20, and 22 weeks.
- PFAS compounds included 5 carboxylic acids (4-9 carbon) and 6 sulfonic acids (4-8 carbon + 2 branched PFOS isomers).

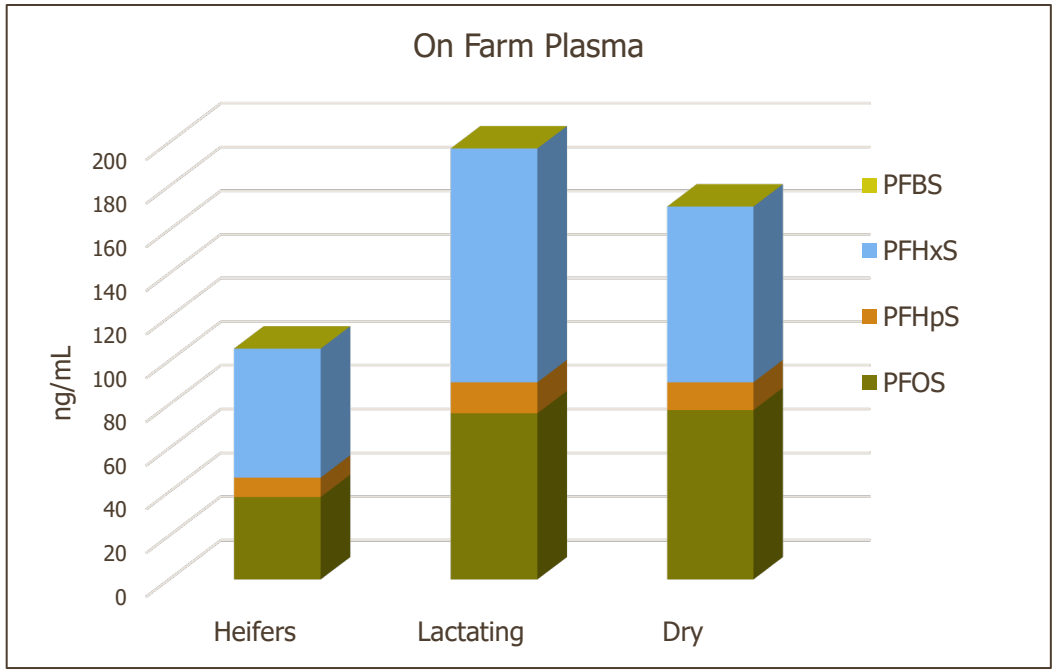
On Farm Analyses
Water and Feed

- **Highest concentrations in water were PFHxS and PFHxA, followed by PFOS and PFOA.**
  - PFNA was <LOD.
- **Highest average concentrations in silage were PFHxA, PFOS, and PFHxS followed by PFBS and PFOA.**
  - Not all silage samples tested had quantifiable levels of all compounds analyzed.
  - PFBA was not measured.
  - PFNA was <LOD.
  - PFHpS was only quantifiable in one sample.



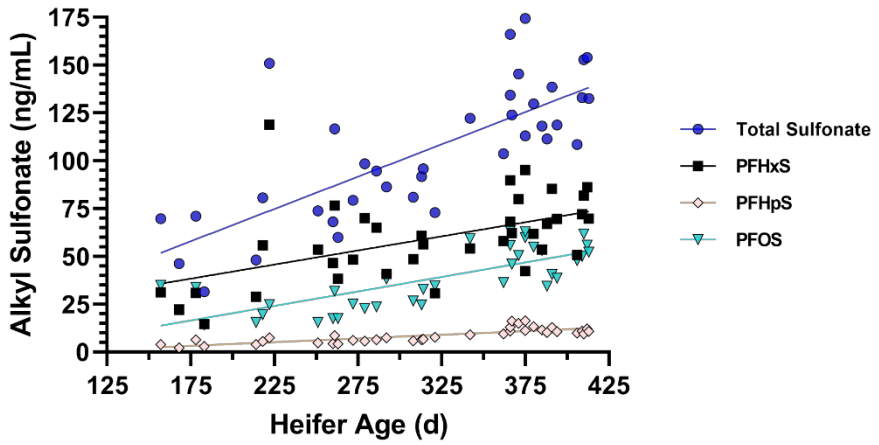
On Farm Analyses Plasma

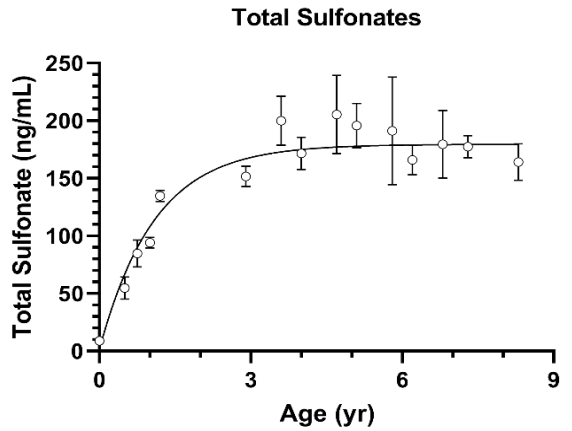
- **No PFCAs were quantifiable in plasma samples** taken on farm even with the high exposure from water and feed.
- PFBS was not quantifiable in plasma.
- **PFHxS, PFHpS, and PFOS were quantifiable in all animals sampled**.
  - PFHxS and PFOS had the highest concentrations in plasma.

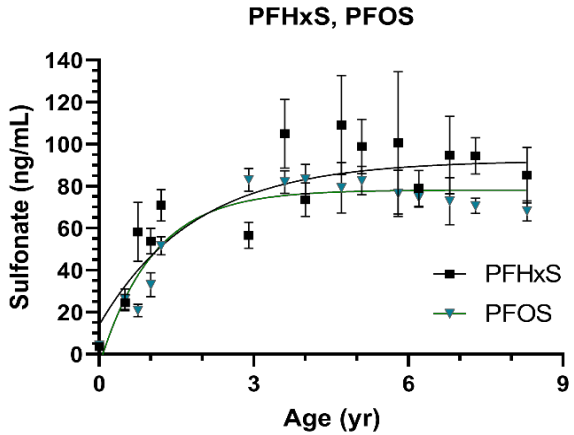


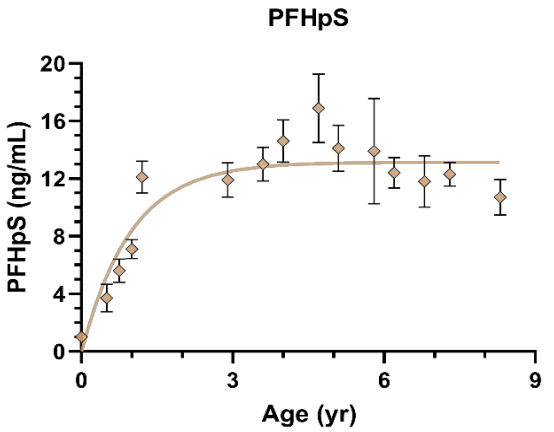
On Farm Analyses
Age and Steady State

- **The larger plasma concentration variation observed in heifers was mainly due to animal age.**
- Heifers ranged from <6 months to 14 months.
- **Plasma steady state levels of total PFSAs were estimated to be achieved between 1.5 to 3 years of age.**



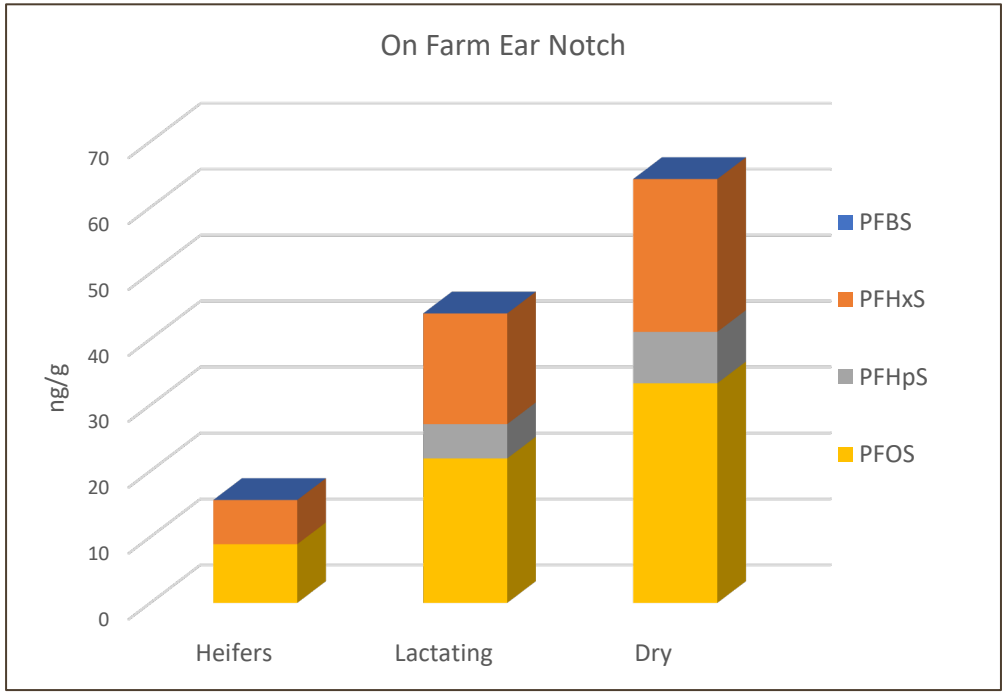






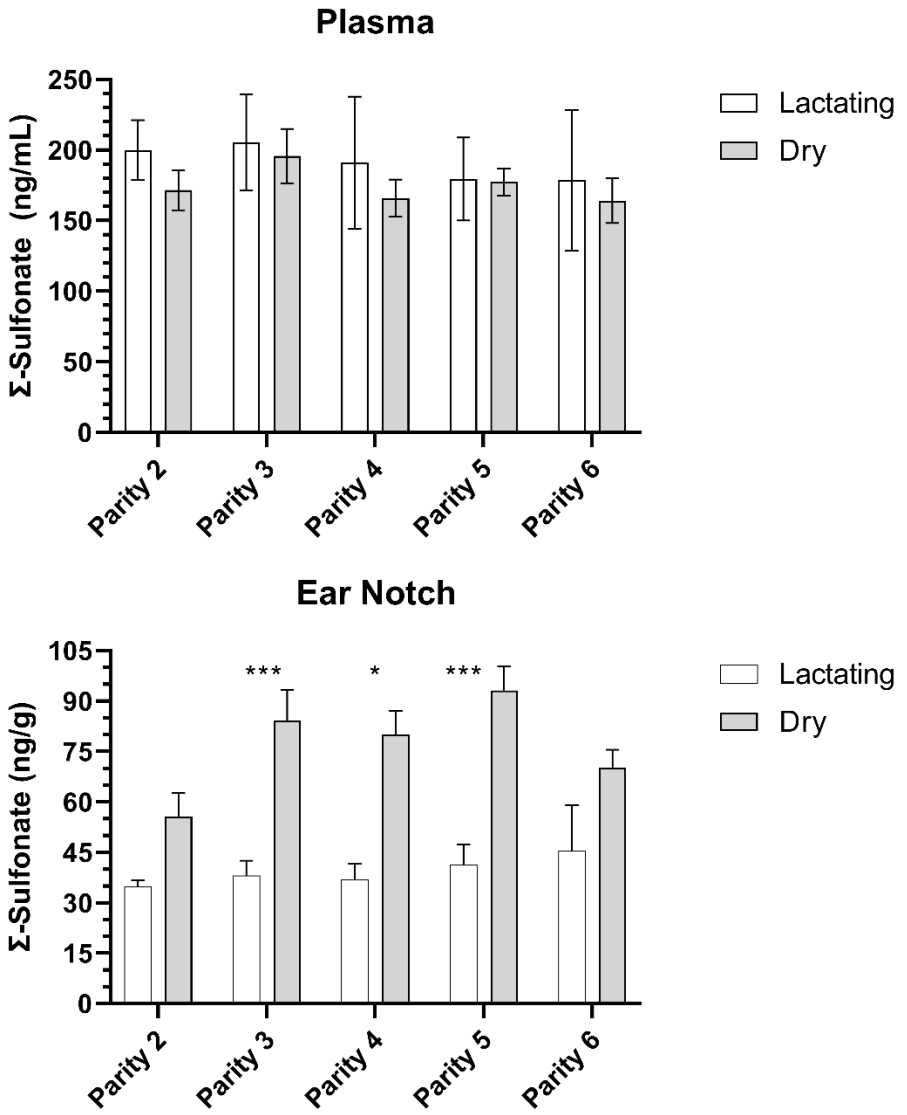
On Farm Analyses
Ear Notch

- For PFCAs, only PFOA was quantifiable at low concentrations in ear notch samples of some heifers (n=34), dry cows (n=20), and lactating cows (n=27).
- PFBS was not quantifiable in ear notch samples.
- **PFHxS and PFOS were quantifiable in all heifers, dry, and lactating cows sampled, while PFHpS was only quantifiable in some dry (n=66) and lactating cows (n=14).**
  - PFHxS and PFOS had the highest concentrations in ear notch.
- **Ear notch samples could be used for biomonitoring purposes where blood collection is not as practical.**



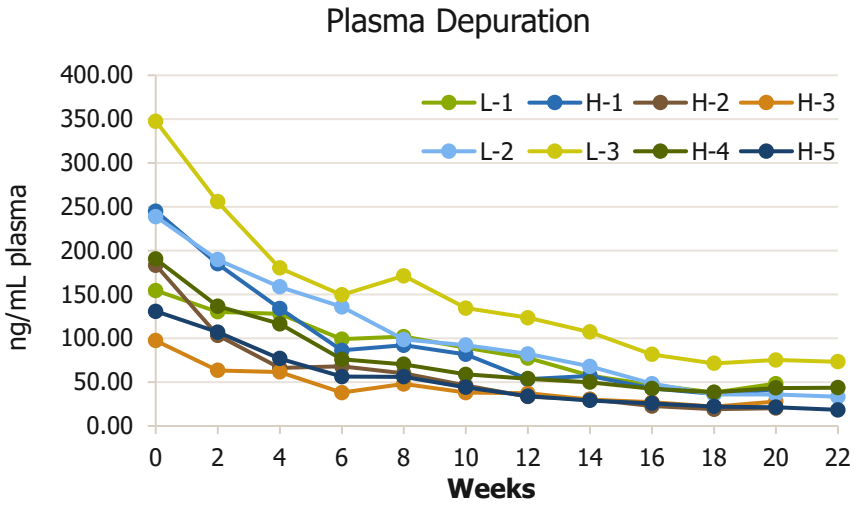
Parity and Lactation Status

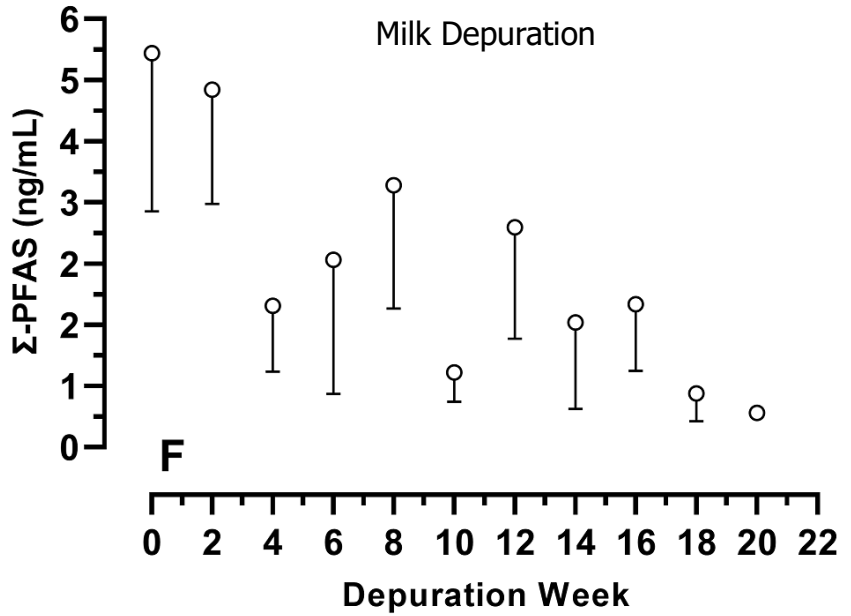
- Neither parity or lactation status affected (P>0.05) total PFSA concentrations in plasma.
- Parity did not affect (P>0.05) total PFSA concentrations in ear notch.
- **Lactation status significantly affected (* P<0.05, ***P<0.0001) total PFSA concentrations in ear notch samples**.
  - Within parities 3,4, and 5, lactating cows had significantly lower total PFSA concentrations in ear notches than dry cows.



Depuration Analyses
Plasma and Milk

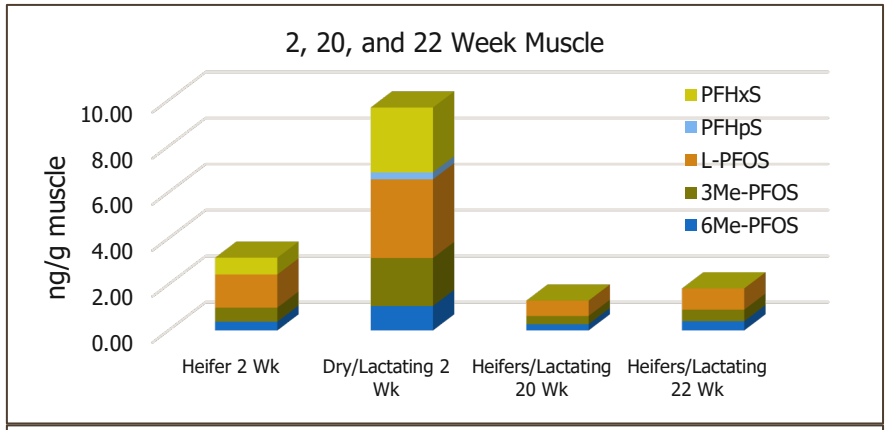
- **None of the carboxylic acids (4-9 carbon chain) were detected in plasma.**
- **Sulfonates longer than 4 carbons (6-8 chain lengths) were accumulated in plasma.**
  - Concentrations decreased during the 22-week depuration period to less than half the initial plasma concentration.
- **The same compounds were detected in milk at low ppb levels, however concentrations over the 22-week depuration period were much more variable.** In general, the concentrations trended downward.

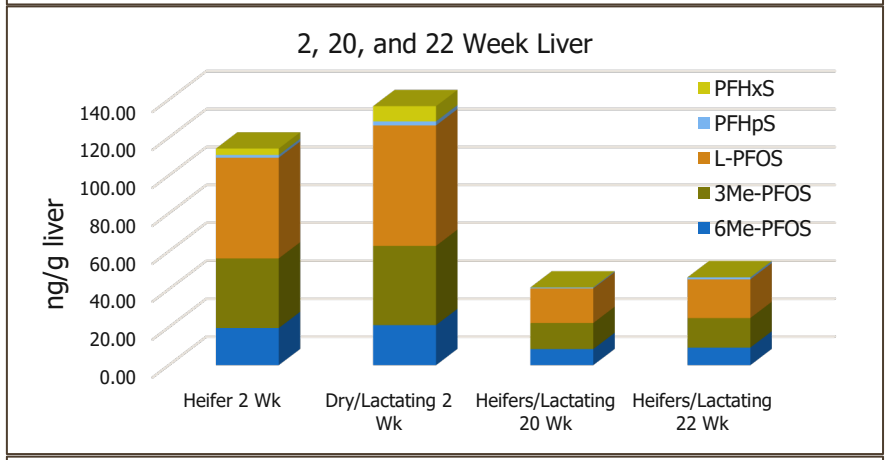


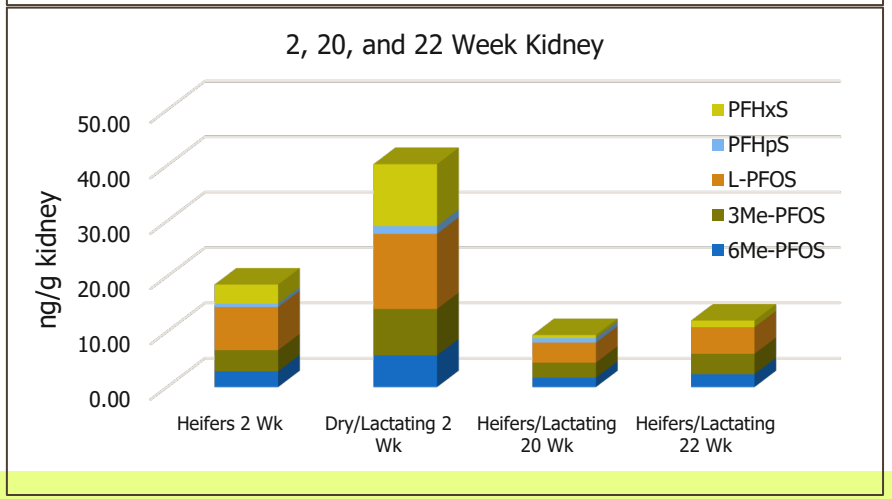


Depuration Analyses Tissues

- **Carboxylic acids (4-9 carbon chain) analyzed were not found in detectable quantities in muscle, liver, or kidney.**
- **Sulfonates longer than 4 carbons (6-8 chain lengths) were accumulated in muscle, liver, and kidney but decreased overall in concentration over the 22-week depuration.**
- By week 22, only the 3 PFOS isomers had detectable concentrations in muscle for heifers and lactating cows but individual isomers were below 1 ppb each.
- Over the 22-week depuration liver and kidney sulfonate concentrations decreased by 50-75% but were still elevated in the low-mid ppb.







USDA Efforts for PFAS

- USDA Agricultural Research Service - PFAS Research in agriculture including soils and livestock.
- USDA Food Safety and Inspection Service - PFAS testing in meat and poultry (beef, pork, chicken, and catfish).
- USDA Natural Resources Conservation Service - providing soil and water testing through Conservation Evaluation and Monitoring Activity 209. Funding to academia and other US agencies for additional research.
- USDA Farm Service Agency - has opened Dairy Indemnity Payment Program for loss of dairy cows due to PFAS contamination.
- Many USDA agencies along with other US agencies provide consultation services and testing when appropriate to states.

Other US Efforts for PFAS

- US EPA health advisory
  - PFOA 0.004 ppt
  - PFOS 0.02 ppt
- US EPA proposed Drinking Water Standards among other proposed regulations.
  - PFOA 4.0 ppt
  - PFOS 4.0 ppt
- Other efforts by US agencies include but not limited to CDC, DOE, DoD, USGS, FDA, ASTDR, NIH, NIEHS, NIST, NOAA, and OSTP.
- Interagency working groups also meet frequently to discuss PFAS issues.
- https://www.whitehouse.gov/wp-content/uploads/2023/03/CEQ-PFAS-Report-March-2023.pdf
- Up to 29 states have water PFAS screening levels. Some of the guidance follows what EPA has set forth. Additionally, some states also have screening levels for soils.

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