SURVEY OF PFAS COMPOUNDS IN EDIBLE FISH SPECIES IN CANADA

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MERCIFULLY BRIEF INTRODUCTION TO PFAS

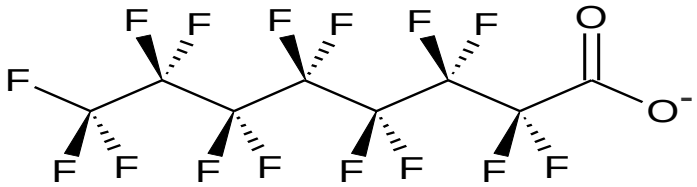
What are PFASs?

PFASs are **P**er- and **P**oly**F**luorinated **A**lkyl **S**ubstances. Exclusively anthropogenic, thousands of individual compounds.

Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophillic end group – overall molecule relatively polar.

Diverse range of compounds with a wide variety of chain lengths (MW) and end groups.

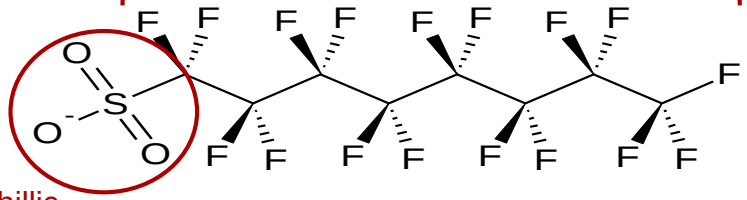
Carboxylate



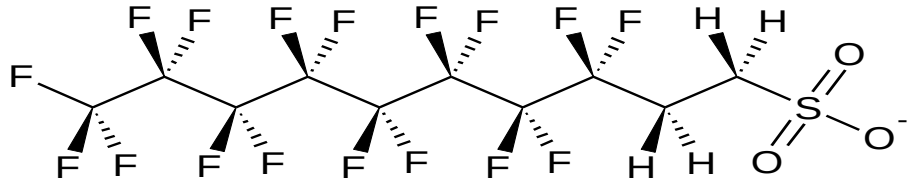
Perfluorooctanoic acid
- PFOA
- Teflon®

Hydrophobic

Hydrophillic



Perfluorooctane Sulfonate
- PFOS
- Scotchguard®



Precursor

8:2 Fluorotelomer sulfonate
- 8:2 FTS

PFAS ENVIRONMENTAL FATE & TRANSPORT

FATE

Shorter (<C8) PFAS: highly resistant to degradation & are persistent.

Higher MW PFAS precursors may break down slowly (soil microbes) to the shorter PFAS.

TRANSPORT

PFAS <C8: water soluble and are transported readily through the subsurface to rivers/streams etc.

PFAS ≥C8: bind tightly with soil with the highest MW PFAS having the highest binding affinity.

- Soil bound PFAS typically don't move more than a few cm down into a soil subsurface.
- Transport is primarily by movement of soil particles in the air or water.

Natural Resources Conservation Service - New Mexico, U.S. Department of Agriculture. [Public domain]

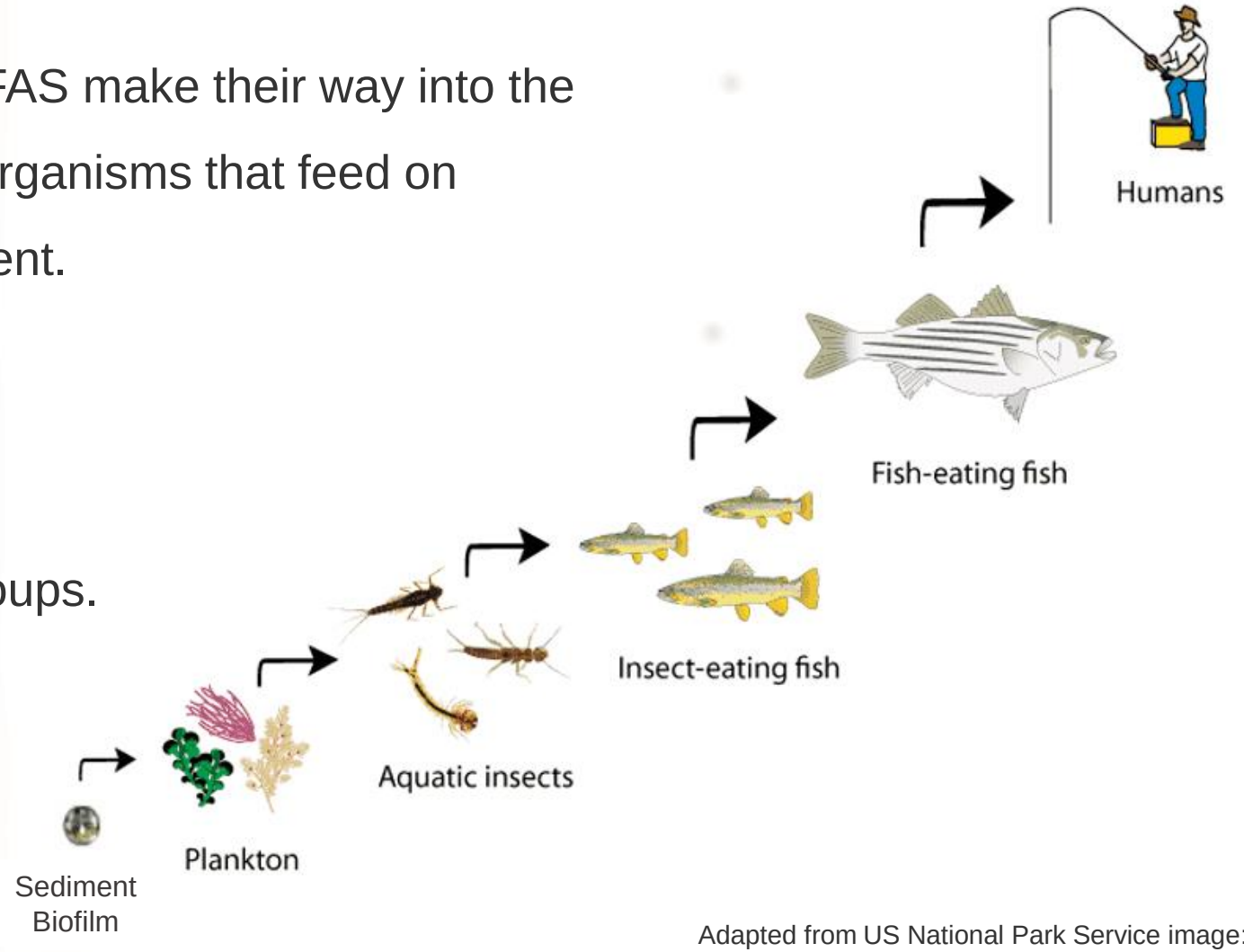
PFAS BIOMAGNIFICATION

The more bioaccumulative (≥C8) PFAS make their way into the food chain primarily through lower organisms that feed on organics associated with soil/sediment.

Greatest Biomagnification:

Longer CF_2 chains.

Sulfonate (vs. carboxylate) head groups.



Adapted from US National Park Service image:
https://www.nps.gov/subjects/air/humanhealth-toxics.htm

PFAS HUMAN EXPOSURE & TOXICITY KNOWLEDGE TIMELINES

1968: Human exposure (blood serum) recognized publicly.

1978: Immunotoxicity discovered in monkeys but not made publicly available.

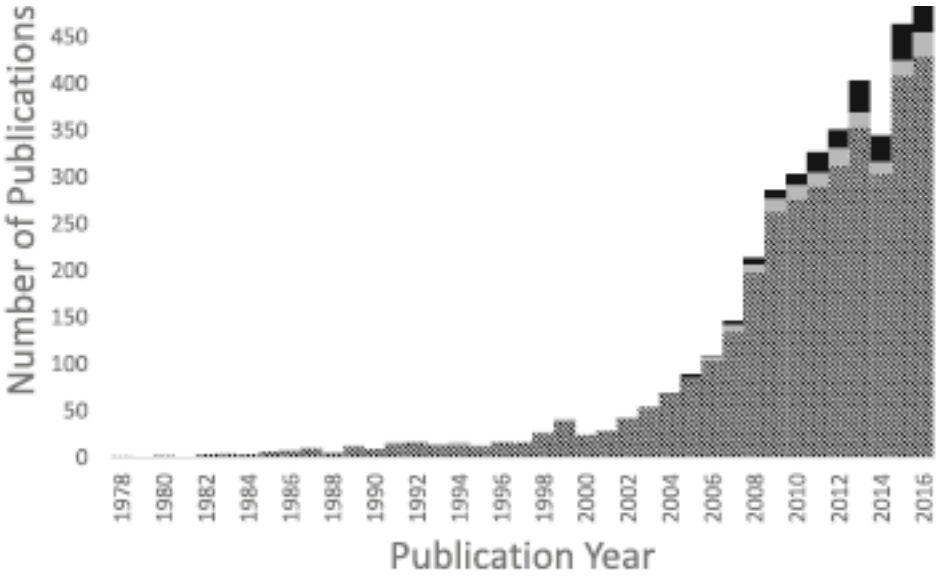
Much of the knowledge of human ADME and immunotoxicity remained unpublished until early 2000s.

2003: PFAS found in donated blood: American Red Cross.

2008: First published study showing immunotoxicity.

Grandjean, Environmental Health, 2018, 7, 62

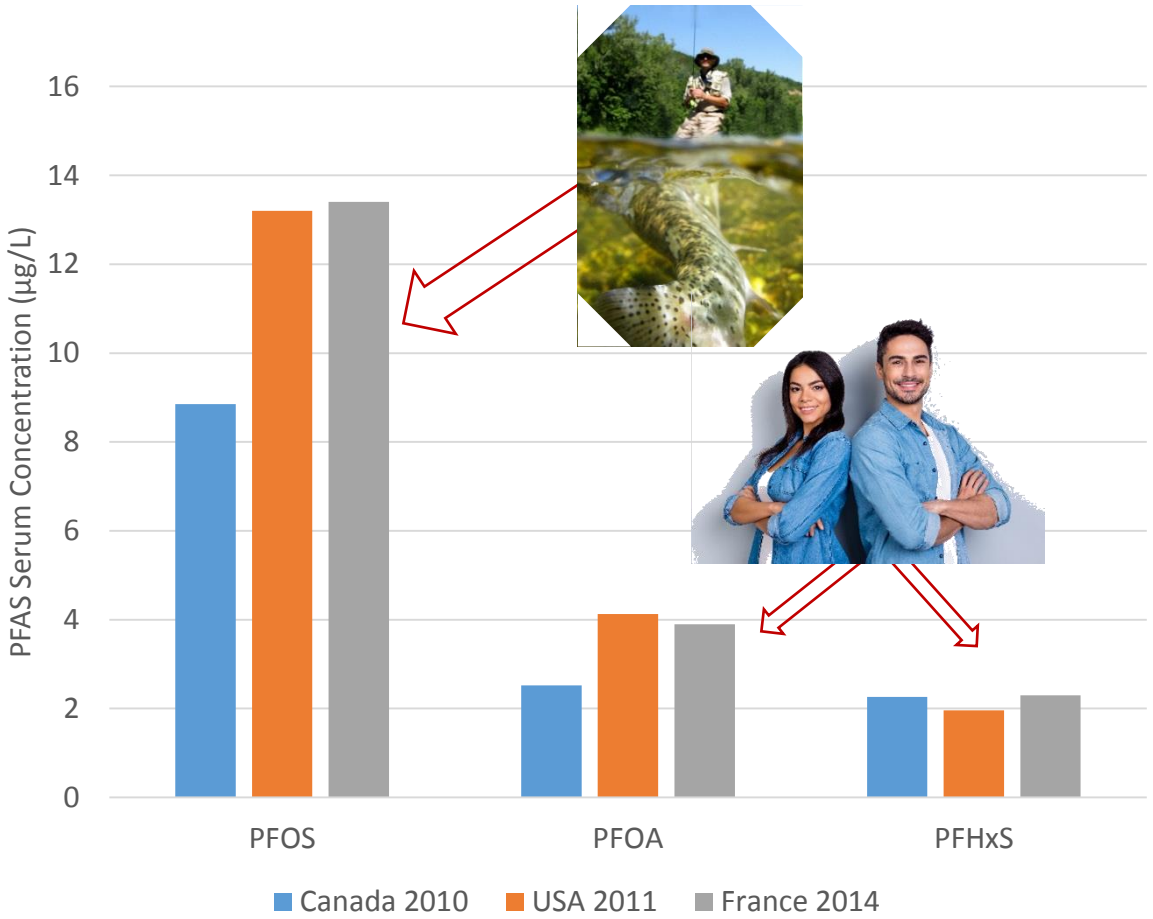
Publications on PFAS environmental science, toxicology, public, environmental or occupational health



Take-aways:

- PFAS do not follow the typical route to chronic toxicity, not lipophilic, probably not carcinogenic.
- Standard models of toxicity generally failed to identify the hazard.
- PFAS are “proteinophilic” – they bind to the body’s proteins/enzymes

PFAS IN HUMAN BLOOD – 2010 to 2014



PFOS found at highest levels in all three studies.

Relative concentrations in the French study:
PFOS>PFOA>PFHxS>PFNA>PFHpS>PFDA

Conclusions of the French Study:

- Consumption of freshwater fish (>10 meals/yr) is a significant contributor to total PFAS body burden.
  - No correlation with marine fish consumption was observed
- PFOS concentration mostly determined by fish consumption.
- PFOA and PFHxS concentration mostly determined by gender.
- Age and geographical location (near rivers) also determinants.

Health Canada, Report on Human Biomonitoring of Environmental Chemicals in Canada 2007-2009, 2010.
K. Kato et al. Environmental Science & Technology, 2011, 45, 8037-8045.
S. Denys et al. Toxicology Letters. 2014, 231, 233-238.

GENDER AND AGE CORRELATIONS

GENDER

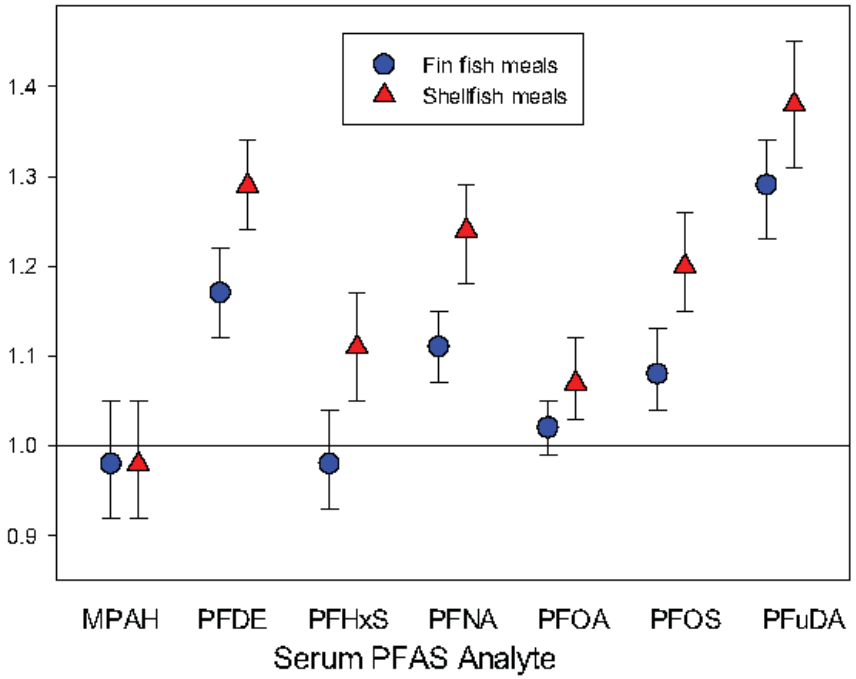
Canadian Population Data: Health Canada 2010

AGE

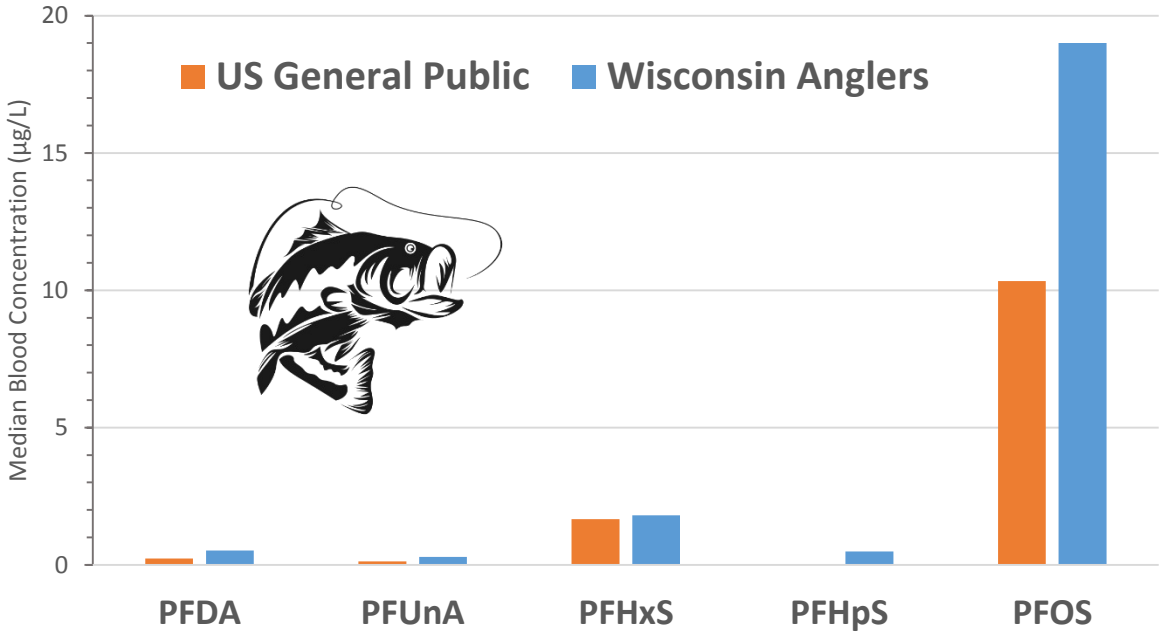
French Population Data: Denys et al. 2014

FISH CONSUMPTION, PFAS BLOOD LEVELS AND HUMAN HEALTH OUTCOMES

Ratios: Serum PFAS concentrations of US fish consumers vs. non-consumers.



PFAS blood concentrations:
Wisconsin Anglers vs US general population



Blood PFAS in anglers associated with diabetes and high cholesterol

Christensen et al. Environment Research, 2017, 154, 145-151.
Christensen et al. Environment International, 2016, 92, 312-318.

2018 U.S. FISH PFAS SURVEY RESULTS

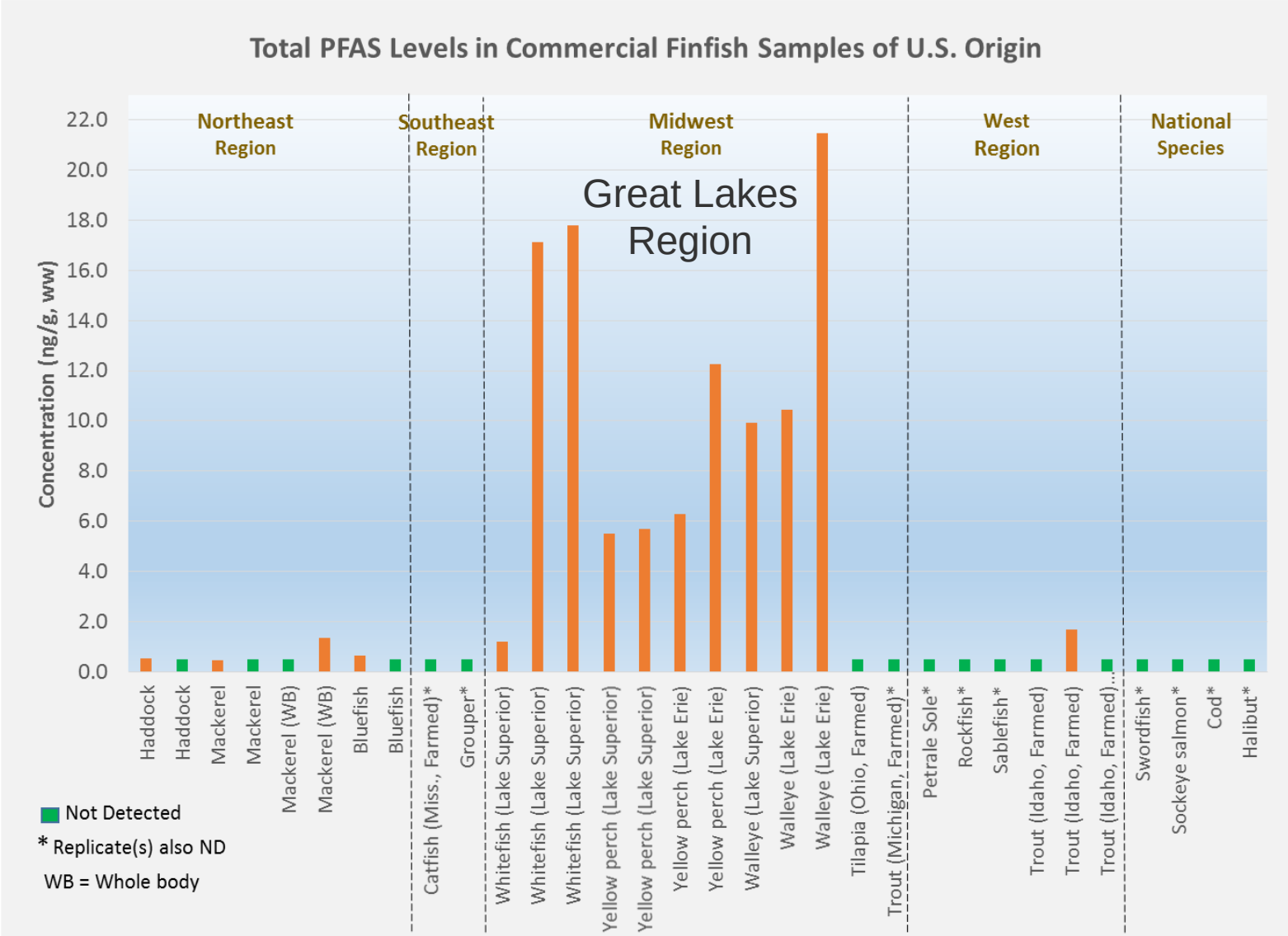
Most fish consumed by US population are low to ND for total PFAS

Highest concentrations found in fish from Great Lakes waters

- Farmed trout from Michigan and Ohio were <DL (0.5 ng/g)

Fish imported from Canada, China, Norway and Central/South America were also near or below DL

Ruffle, B., et al. AECOM USA, presented at the Battelle Sediments Conference, February 2019.



STUDY BACKGROUND

Fish collected by Bureau Veritas staff and clients, Summer 2019.

Brook Trout

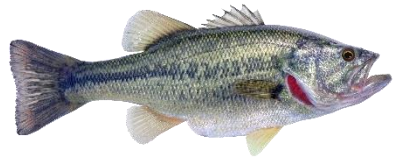
Rainbow Trout

Salmon

Yellow Perch

Northern Pike

Six regions: Nova Scotia, Quebec, Southern Ontario, Ontario Near North, Western Ontario, BC Pacific



Bass

Mostly finfish, mostly wild caught, total of 30 fish. Submitted in food grade plastic bags.

Fish filleted, skin removed, tissue portion tested, minimum 100g.

Whitefish

ANALYTICAL METHOD DETAILS

1. Sample homogenized, isotopically labeled internal standards added.
2. Extracted using an organic solution under basic conditions.
3. Cleanup and concentration by solid phase extraction.
4. Reverse phase liquid chromatography column prior to detection using tandem mass spectrometry (LC/MS/MS).
5. Each perfluorinated compound is quantified by isotope-dilution method using a multi-point calibration curve.

Analysis of 32 PFAS compounds:

- Short and long-chain Carboxylates and Sulfonates, Precursors, and Replacement Compounds.

PFAS	# C	Group
PFBA	4	Carboxylate
PFPeA	5	Carboxylate
PFHxA	6	Carboxylate
PFHpA	7	Carboxylate
PFOA	8	Carboxylate
PFNA	9	Carboxylate
PFDA	10	Carboxylate
PFUnA	11	Carboxylate
PFDoA	12	Carboxylate
PFTrDA	13	Carboxylate
PFTeDA	14	Carboxylate
PFBS	4	Sulfonate
PFPeS	5	Sulfonate
PFHxS	6	Sulfonate
PFHpS	7	Sulfonate
PFOS	8	Sulfonate
PFNS	9	Sulfonate
PFDS	10	Sulfonate
PFOSA	8	Precursor - sulfonamide
MeFOSA	9	Precursor - sulfonamide
EtFOSA	10	Precursor - sulfonamide
MeFOSE	9	Precursor - sulfonamidoethanol
EtFOSE	10	Precursor - sulfonamidoethanol
MeFOSAA	9	Precursor - sulfonamidoacetate
EtFOSAA	10	Precursor - sulfonamidoacetate
4:2-FTS	6	Precursor - fluorotelomersulfonate
6:2-FTS	8	Precursor - fluorotelomersulfonate
8:2-FTS	10	Precursor - fluorotelomersulfonate
HFPO-DA	6	Replacement - GenX
ADONA	7	Replacement
9Cl-PF3ONS	8	Replacement - F-53B Component
11Cl-PF3OUdS	10	Replacement - F-53B Component

RESULTS – TOTAL PFAS IN FISH BY REGION

Median total PFAS concentration 3.5 ng/g

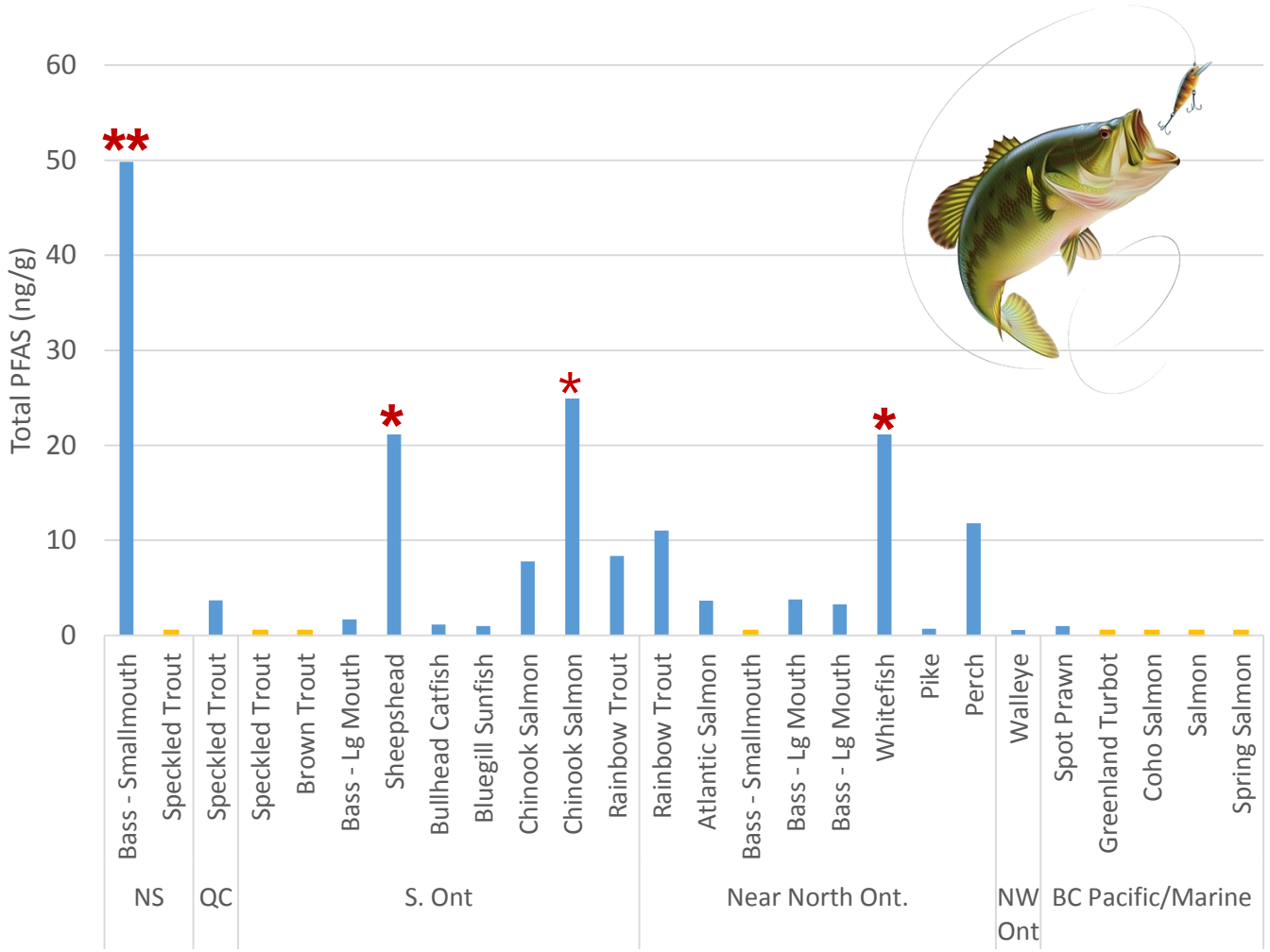
- Consistent with US data

Three fish (*) equivalent to highest concentrations in US data

One fish (**) 2x the highest level in the US

Marine finfish (Salmon) and a few freshwater fish <DL (yellow bars)

Observed concentrations likely relate to both location and species habitat/diet



RESULTS – PFAS DETECTED

Distribution of PFAS observed consistent with previous studies.

- Median PFOS concentration lower than observed in US studies.
- Levels of C12 and C13 carboxylates and C10 sulfonamide are higher than in US studies.
- Highest PFOS concentration (39 ng/g) meets the Michigan Department of Health advisory for a maximum of 2 meals/month.

FISH ROUTES OF EXPOSURE

1) Absorption of free PFAS in water via respiration (shorter chain PFAS)

Short chain PFAS are less likely to accumulate

2) Benthic organisms accumulate long-chain PFAS by exposure to sediment-sorbed PFAS during feeding

Sediment-sorbed PFAS have longer CF_2 chains and are more likely to be sulfonates; i.e. more bioaccumulative PFAS

Benthic microbiota and associated **biofilms** are the primary producers in the sediment ecosystem.

Benthic invertebrates, mollusks, crustaceans depend on benthic microbiota for food.

Bottom-feeding fish have significant exposure to long-chain PFAS.

LOCATION / DIET / HABITAT RELATIONSHIPS

Rainbow Trout vs Salmon:

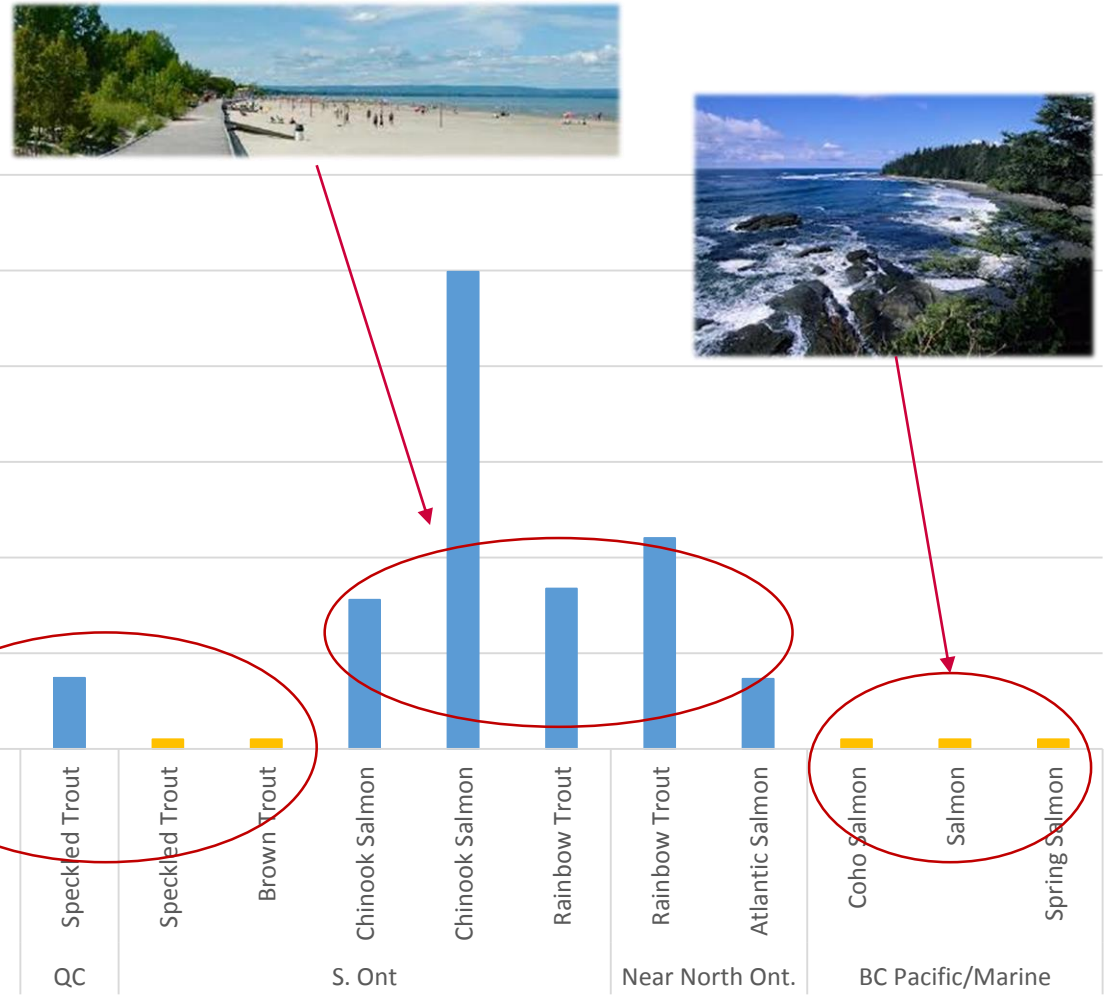
Rainbow Trout and Pacific Salmon are closely related, both preferring to eat crustaceans, insects and small fish.

Significant difference in PFAS load. Rainbow Trout and freshwater Salmon caught in urbanized areas of Ontario Great Lakes. Pacific Salmon caught in Pacific Ocean.

Speckled Brook & Brown Trout:

Primarily eat insects.

Low PFAS load possibly due to diet as two of these were from highly urbanized areas and two were from more remote locations.



LOCATION / DIET / HABITAT RELATIONSHIPS

Nova Scotia Smallmouth Bass:

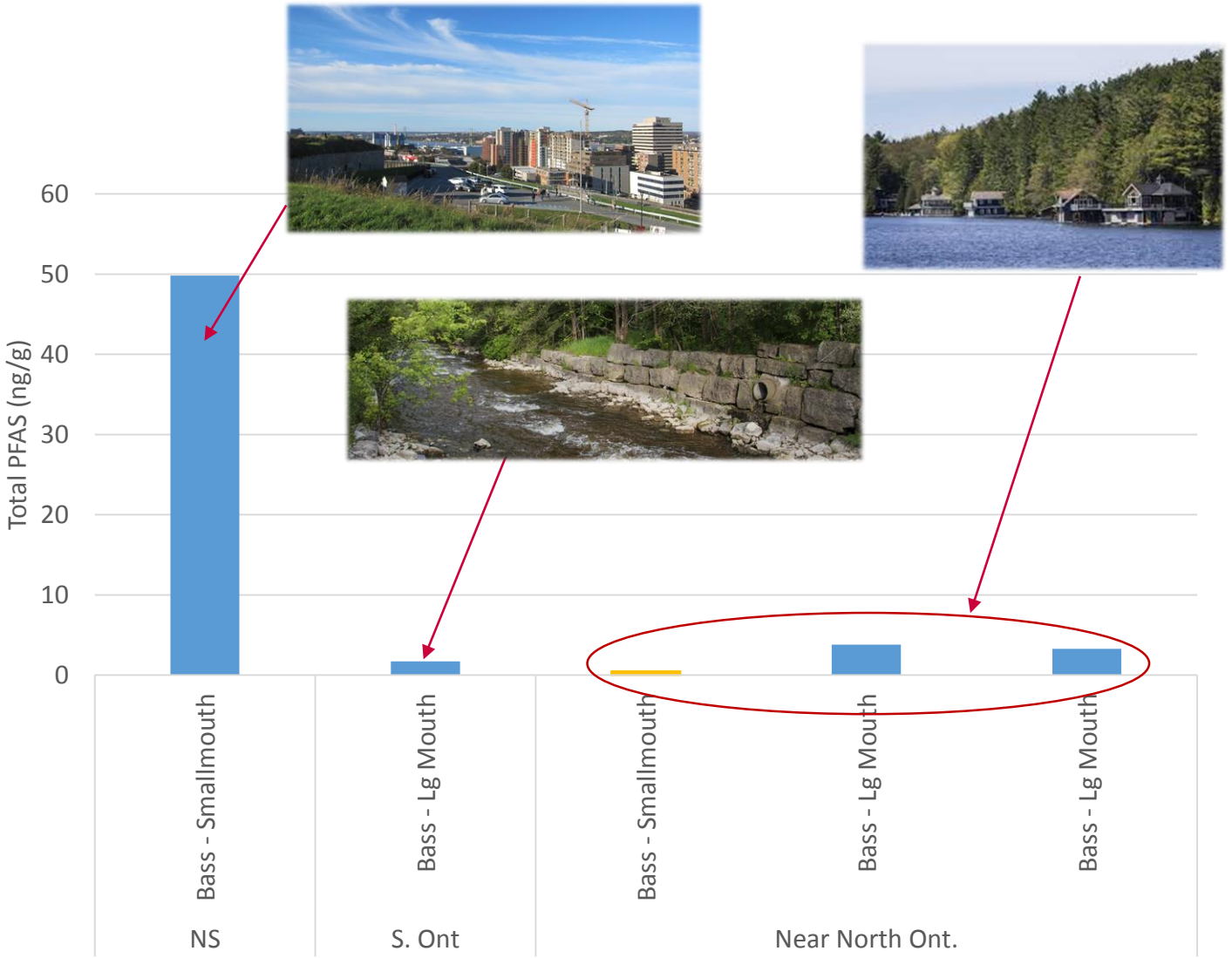
Urban freshwater lake near Halifax, long history of urbanization and industry

Crayfish (benthic) are important in diet

Ontario Bass:

Lakes in thinly populated urban areas with minimal industry.

(Largemouth Bass: primarily large fish eaters.)



LOCATION / DIET / HABITAT RELATIONSHIPS

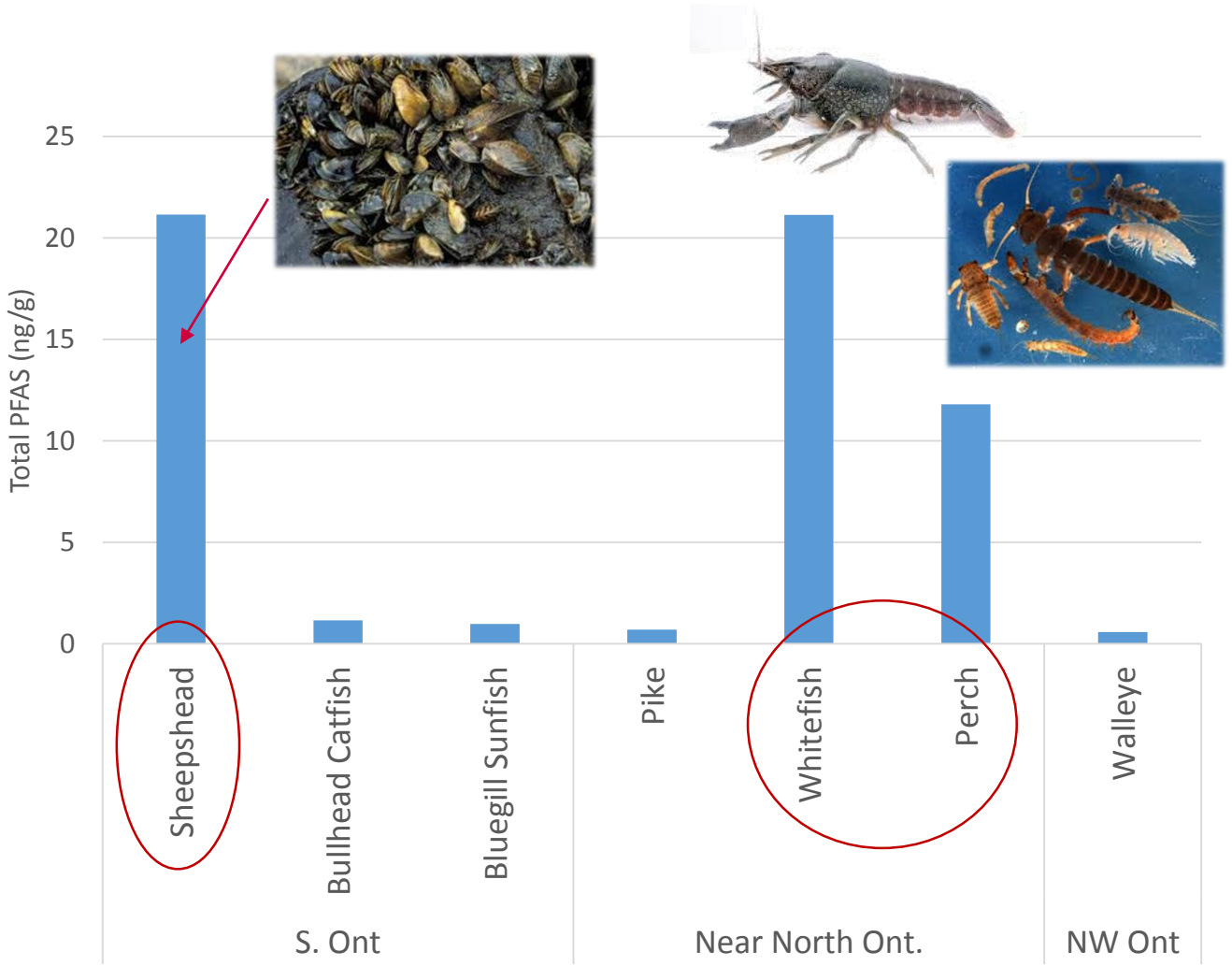
Whitefish and Perch:

Whitefish diet: mollusks and benthic invertebrates

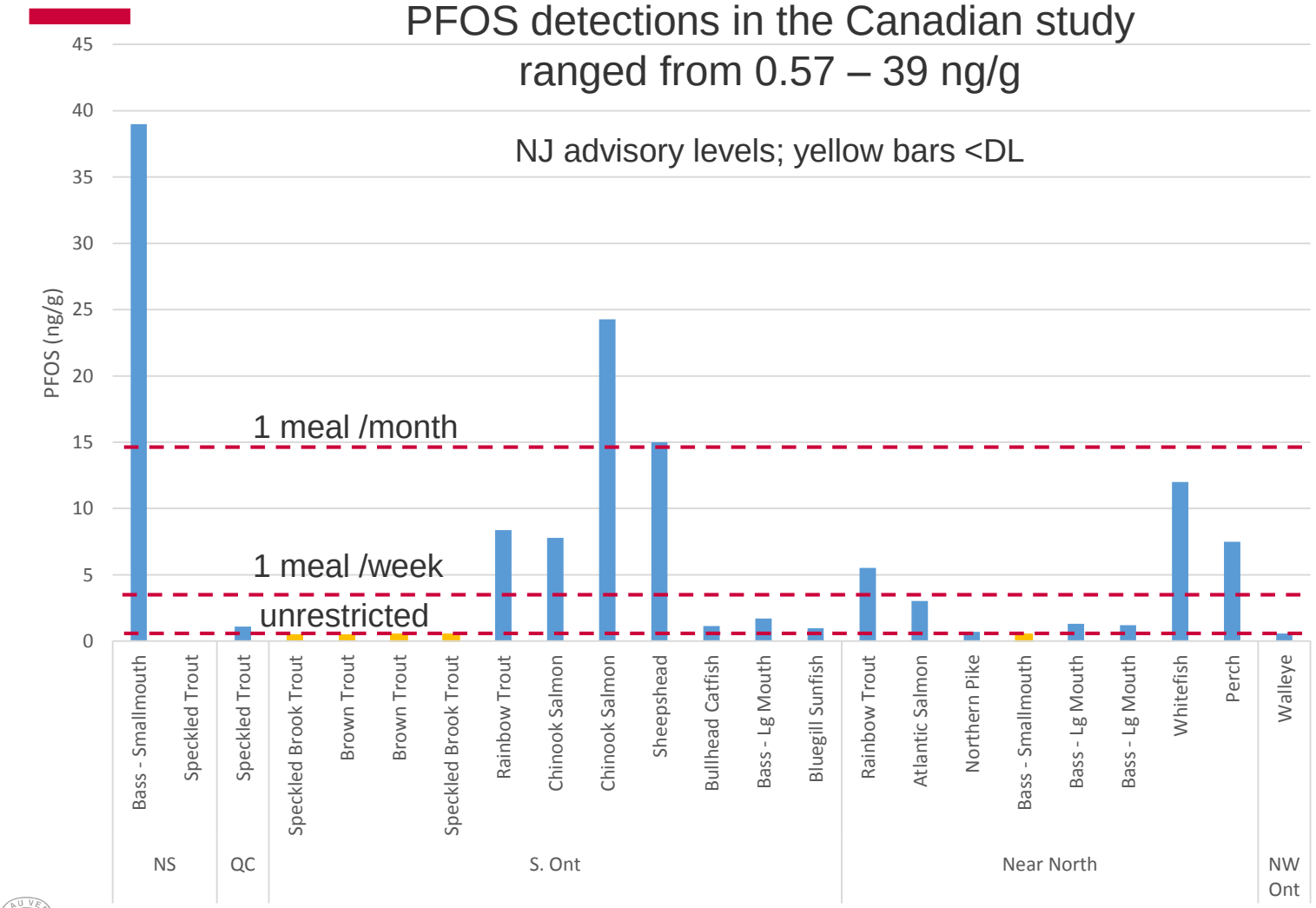
Perch diet: omnivorous bottom-feeders

Sheepshead:

Diet: benthic species, mollusks: zebra mussels



PFOS LEVELS VS N.J. CONSUMPTION ADVISORY



Some US states have published consumption advisories for PFOS fish tissue concentrations.

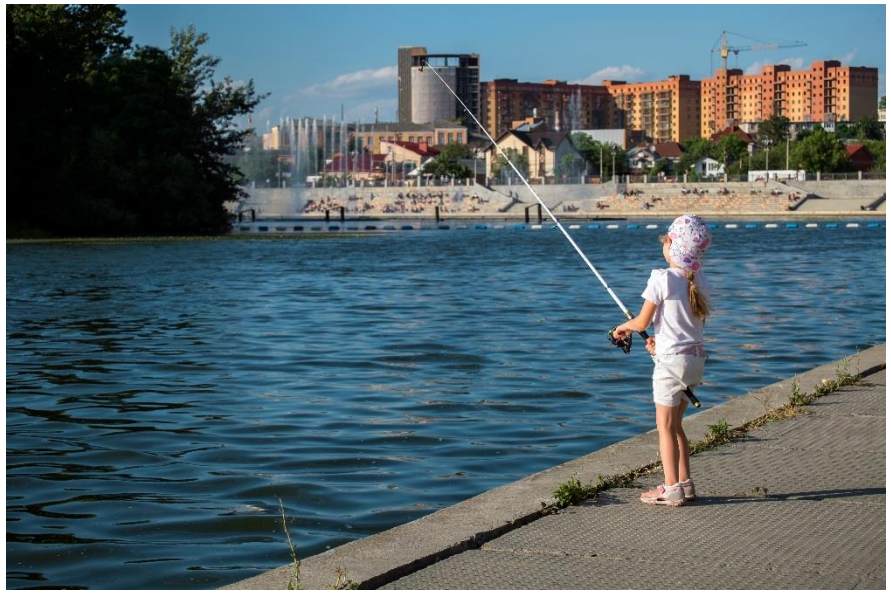
NJ and Minnesota advisories are most current (2018):

- Unrestricted: 0.56 – 10 ng/g
- 1 meal /week: 3.9 – 50 ng/g
- 1 meal /month: 17 – 200 ng/g
- No consumption: 204 - >200 ng/g

PARTING THOUGHTS

1. Food/fish is the major source of human exposure to PFAS.
2. Canadian freshwater fish appear to have similar to higher total PFAS concentrations than those from the US.
3. Benthic-feeding fish in urban-impacted environments appear to have the highest PFAS levels.
4. Sequestering PFAS in soil/sediment may not be an appropriate remedial approach.
5. Current toxicity measures are not good predictors for PFAS toxicity; problematic for PFAS risk assessment.
6. Fish are a good predictor of human exposure to PFAS≥C8.

Fish - the PFAS "canary in the coal mine"



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