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POSTER SESSION 3.04

Consideration of Site-Specific Conditions and Food Web Structures in Per- and Polyfluoroalkyl Substances (PFAS) Bioaccumulation: A Watershed-Scale Case Study

Sagar Thakali (Conshohocken, PA) | Maryann Welsch (Portland, ME) | Gemma Kirkwood (Chelmsford, MA)
Chrissy Puopolo (Chelmsford, MA) | Christine Archer (Manchester, NH) | Heather Loso (Oakland, CA)
Betsy Ruffle (Chelmsford, MA)

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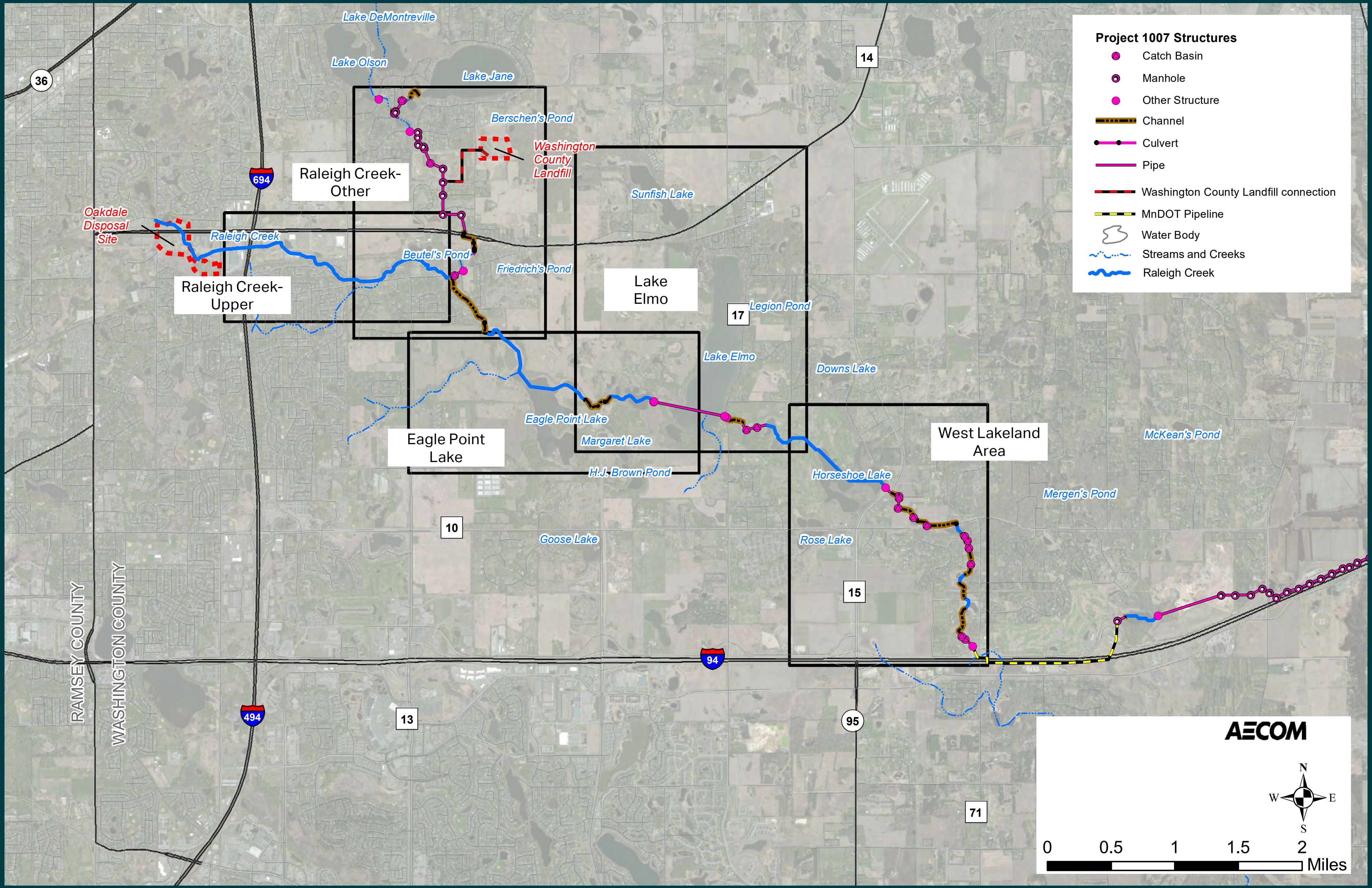
Introduction

- Project 1007 is a 14-mile stormwater conveyance system in the east Twin Cities Metro Area (Minnesota, USA; see Figure 1) that mitigates flooding in the Tri-Lakes area by lowering water levels in Lakes Jane, Olson, and De Montreville and helps improve Lake Elmo water quality. The project area includes a series of open channels, storm sewers, and existing surface water features, and ultimately discharges to the St. Croix River [Minnesota Pollution Control Agency (MPCA), 2022].
- Project 1007 includes two historic per- and polyfluoroalkyl substance (PFAS) disposal sites: the former Oakdale Disposal Site (ODS) and Washington County Landfill (WCL). The ODS is situated in a wetland area which drains to Raleigh Creek. The WCL is located south of the Tri-Lakes Area and discharged to Project 1007, upgradient of the Raleigh Creek confluence via pipe from 1988 to 1995. Although this discharge has been terminated, the residual impacts may remain along the flow path.
- AECOM (2021) performed a PFAS Baseline Ecological Risk Assessment (BERA) for five waterway sections in Project 1007 including Raleigh Creek - Upper, Raleigh Creek - Other, Eagle Point Lake, Lake Elmo, and West Lakeland Area (see Figure 1). Extensive sampling of abiotic media (surface water, sediment, pore water, and foam) and biotic media (aquatic plants, crayfish, snails, amphibians, forage fish, bottom fish, and predatory fish) was conducted in support of the BERA. Altogether 41 PFAS were analyzed, including short and long-chain carboxylates and sulfonates, fluorotelomers, and sulfonamides.
- The overall objective of the current study is to identify site-specific patterns and trends in PFAS bioaccumulation in the 2021 BERA dataset that may be extrapolated for generalities and to different sites.

Figure 1. Project 1007 Overview



Watershed, Habitat, and Food Web

Multiple streams discharge into Project 1007 with Raleigh Creek being one of the largest. The Raleigh Creek headwaters include a wetland area in the ODS that provides a surface water pathway for PFAS to enter Project 1007 at Tablyn Park (see Figure 1). The Project 1007 conveyance system is made up of dams, pipes, weirs, and other features to help convey the surface water runoff from flood-prone areas, reduce flooding throughout the corridor, and improve Lake Elmo water quality. The conveyance system carries water out of the Tri-Lakes area and into Raleigh Creek at Tablyn Park. Water is piped under Lake Elmo and discharges to the east of Lake Elmo. Prior to Project 1007, Eagle Point Lake drained directly into Lake Elmo; Currently, under most conditions, water is piped underneath Lake Elmo. Project 1007 directly discharges to Lake Elmo via a secondary overflow structure. Combined surface water from Project 1007 and Lake Elmo then flows through Horseshoe Lake and a series of ponds and channels (West Lakeland Storage Sites) before being piped to the St. Croix River.

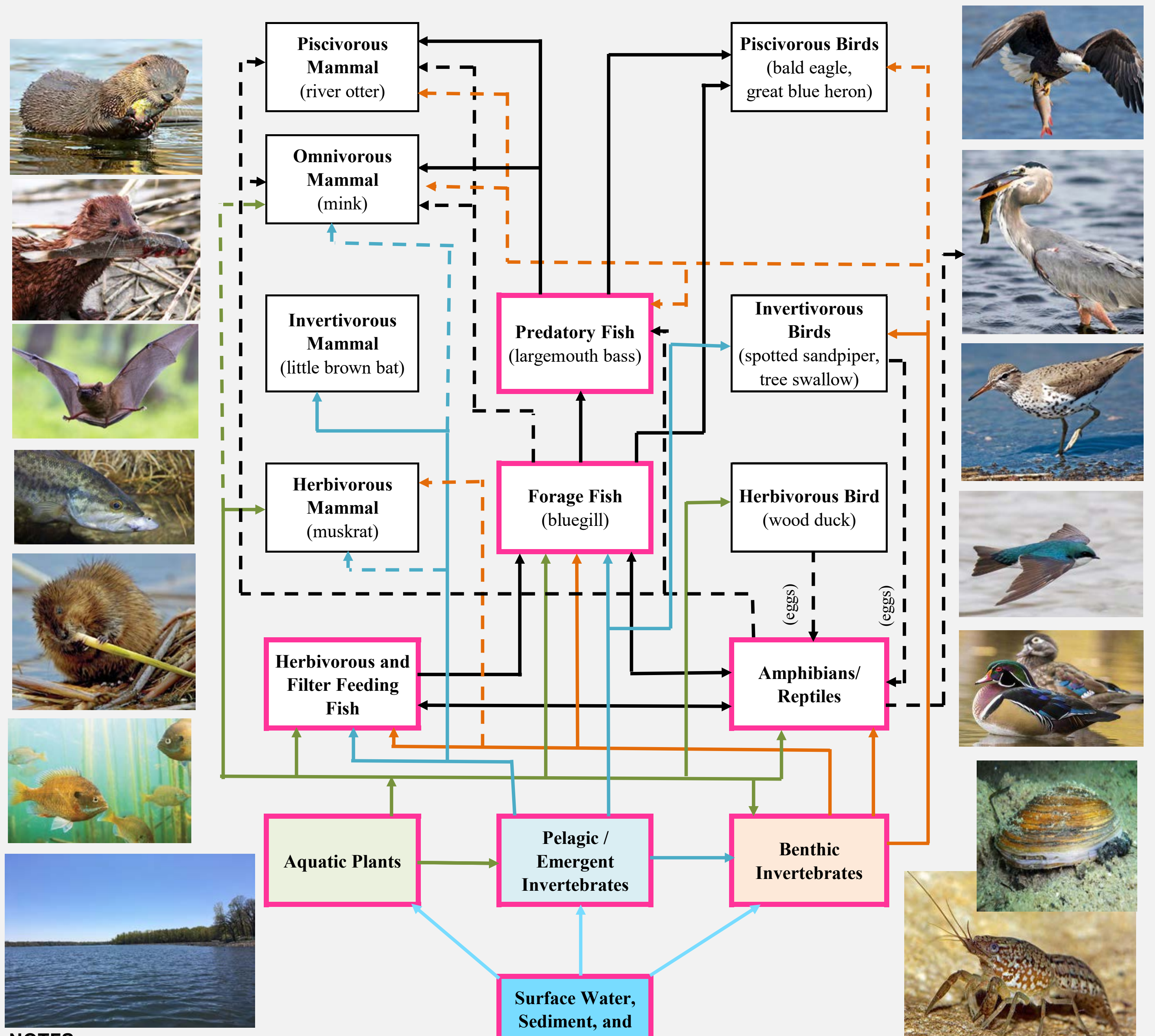
The Project 1007 waterways (wetlands, streams, creeks, channels, ponds and lakes) provide habitat for a variety of plants and animals. The following areas and habitats were the focus of the sampling efforts:

- wetlands and the primary stream channel associated with Raleigh Creek;
- the lake habitats of Eagle Point Lake and Lake Elmo; and
- Horseshoe Lake and the stream and pond habitats of the West Lakeland Storage Sites (referred to as the West Lakeland Area).

Figure 2 depicts the general food web or trophic structure for the watershed. The current study is limited to the aquatic (and benthic) food web. Biotic samples included the following:

- **PLANTS:** Floating aquatic vegetation (FAV, including duckweed); cattails (root and shoot); grasses (including Reed canary grass, Bulrush); other shoreline vegetation (including willow, pale smartweed). Only FAV was used in this current study to represent aquatic plants potentially consumed by aquatic and benthic fauna.
- **BENTHIC INVERTEBRATES:**
  - **Snails:** Opportunistic collection of individual and composite samples
  - **Crayfish:** Primarily individual whole-body samples (one composite sample consisting of two small specimens)
- **AMPHIBIANS:** Green frog tadpole composite samples and adult frog whole-body
- **BOTTOM FEEDING FISH:** Opportunistic collection of whole-body bullhead
- **FORAGING FISH:** Individual and composite whole-body samples; included black crappie, bluegill, cisco, golden shiner, fathead minnow, darter, stickleback, mudminnow, and sunfish
- **PREDATOR FISH:** Individual whole-body, fillet, and parts (whole-body equivalent results discussed in this study); included largemouth bass and northern pike

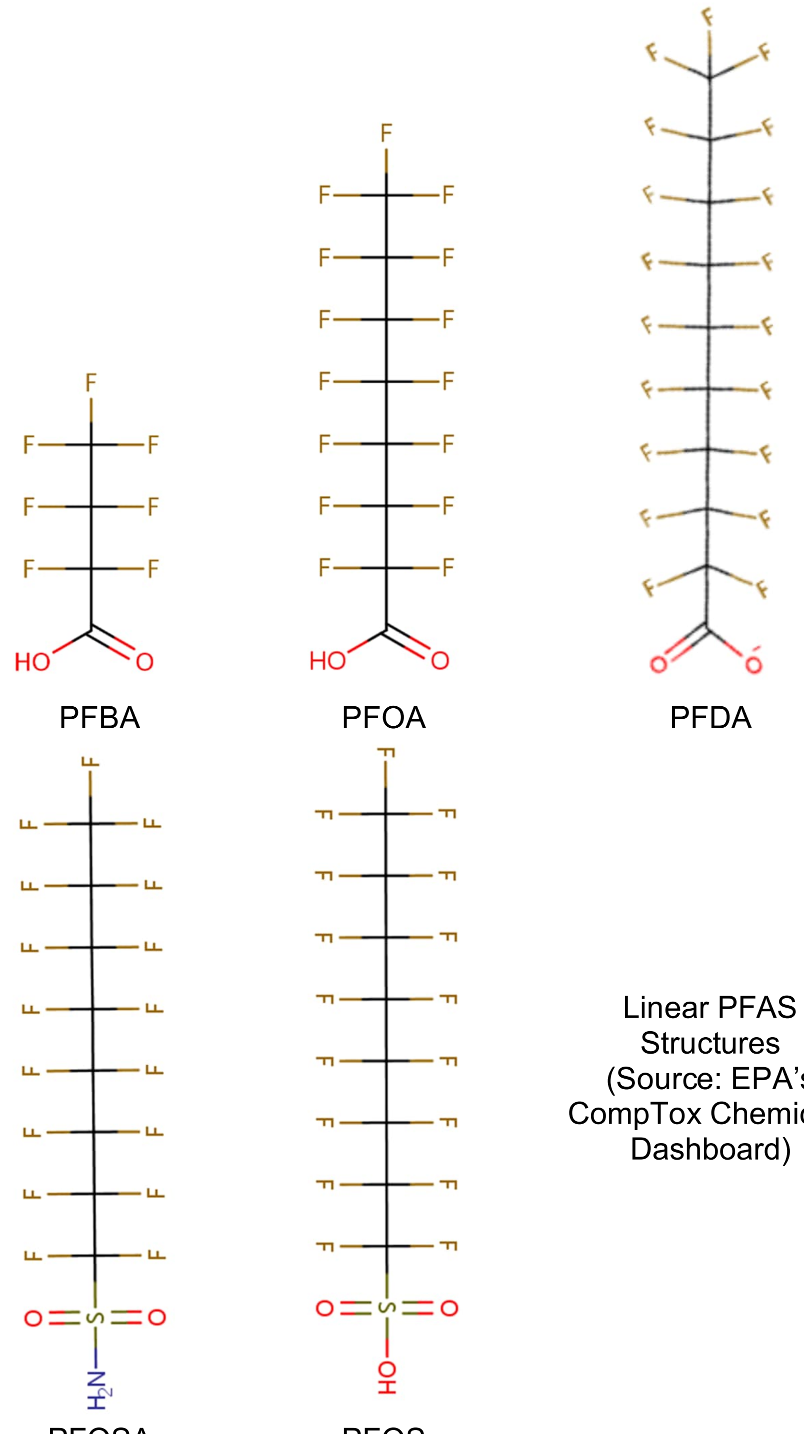
Figure 2. Generalized Aquatic Food Web Structure at Project 1007 Aquatic Habitats



NOTES:
Representative species are shown in parentheses.
Solid line indicates primary dietary items; dashed line indicates additional dietary items.
Aquatic food web considered in this study is highlighed in pink.

General Evaluation Methodology

- PFAS concentrations in organisms were not differentiated for size, age, and species (unless specified otherwise) primarily due to data limitations, but also to reasonably simplify the evaluations in this study.
- Detected PFAS concentrations were primarily considered because this study focuses on observed relationships among various media; treatment and use of non-detects introduce uncertainties in comparing the relative differences in PFAS concentrations among various media.
- PFOS (perfluorooctanesulfonic acid) dominated the PFAS distribution and speciation in abiotic and biotic media. In general, perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), perfluorobutanoic acid (PFBA), and/or perfluorodecanoic acid (PFDA) were also detected at a higher frequency than other PFAS in different abiotic and biotic samples. Based on these general observations and professional judgement, this study focused on PFOS, PFOA, PFOSA, PFBA, and/or PFDA to illustrate comparisons based on PFAS functional groups (PFOS, PFOA, and PFOSA) and carbon chain length in per- or polyflurocarboxylic acid (PFCAs, including PFBA, PFOA, and PFDA).
- Trophic positions (TPs) of the species sampled were not specifically determined in this study. Species TPs were assigned based on the estimated designations for each species or similar species by Burkhard (2021). Other specific methodological details are indicated for corresponding evaluations in this study.



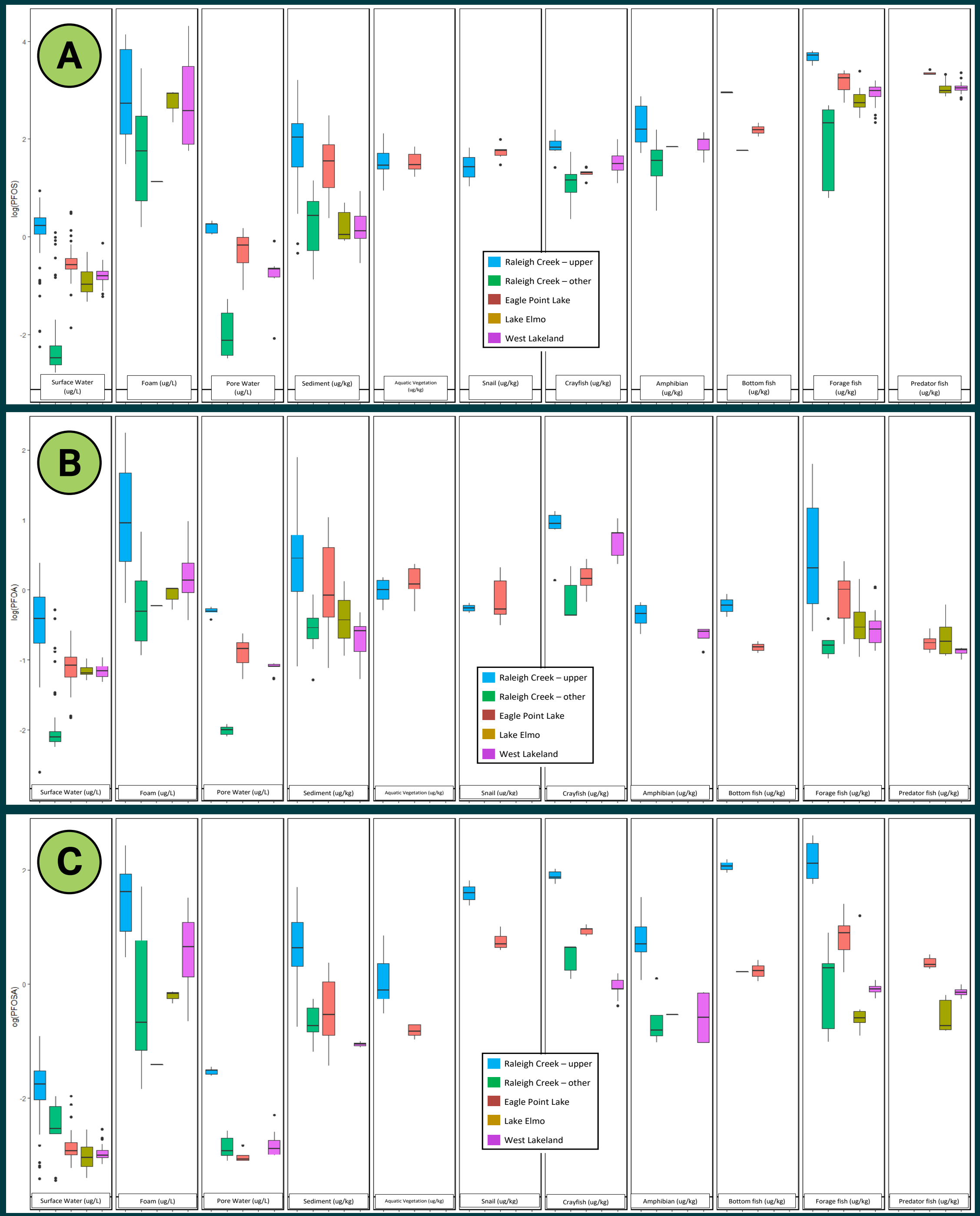
Linear PFAS Structures (Source: EPA's CompTox Chemicals Dashboard)

PFAS Distributions in Abiotic and Biotic Media

Figures 3A, 3B, and 3C show the distributions of PFOS, PFOA, and PFOSA detected in the various abiotic and biotic media across the five general areas ordered from closest to furthest relative to the PFAS source areas (see Figure 1). PFOS, PFOA, and PFOSA each have an eight (8) carbon chain length but with different functional groups. Qualitative observations from Figures 3A, 3B, and 3C include the following:

- **General Differences in PFAS Compounds:**
  - PFOS dominates the speciation and distribution across different media; detected PFOS concentrations in each medium, in general, are approximately two to four orders of magnitude higher than PFOSA and PFOA concentrations, which are comparable. Dominance of PFOS in PFAS speciation and distribution likely reflects the nature of the release as well as compound-specific biogeochemical interactions.
- **General Spatial Patterns in PFAS Concentrations:**
  - In each medium, detected PFAS concentrations generally decrease with distance from the sources, i.e., PFAS concentrations are generally the highest in “Raleigh Creek – Upper” (located closest to the sources) and the lowest in downgradient Lake Elmo and West Lakeland Area; lower detected PFAS concentrations within “Raleigh Creek – Other” may reflect termination of discharge from the upstream/upgradient WCL after 1995.
  - Decreases in detected PFAS concentrations with distance from the source (with the exception of the “Raleigh Creek – Upper” area) are more pronounced in surface water and sediment for PFOS, PFOA, and PFOSA and in biota for PFOSA. Although not displayed in Figure 3, similar trends are observed in concentrations of PFDA but not PFBA; PFBA concentrations in surface water and sediment overlap among different areas. The lack of attenuation with distance from the source for PFBA, which is a short chain PFCA, is likely related to its higher mobility than the long chain PFAS.
- **Patterns in Abiotic Media:**
  - PFAS concentrations in foam are approximately three orders of magnitude higher than in surface water; significant enrichment of PFAS in foam relative to surface water reflects their surfactant properties and may have implications for wildlife exposure via incidental exposures specifically to foam.
  - PFAS concentrations in sediment are approximately two orders of magnitude higher than in pore water (filtered); significant enrichment of PFAS in sediment relative to pore water reflects their partitioning behavior and has implications for fate and transport as well as bioavailability of PFAS with respect to benthic exposure.
- **Patterns in Biotic Media:**
  - PFOS and PFDA (not shown) concentrations generally increase across the TPs, from FAV to predatory fish; a similar pattern is not clear for PFOA, PFOSA, and PFBA (not shown); hence, trophic transfer of PFAS may depend on specific PFAS properties based on function groups and/or carbon chain length.

Figure 3. Overall Patterns in PFAS Concentrations Among Different Media and Waterway Sections: A) PFOS, B) POFA, and C) PFOSA



Associations in PFAS Concentrations Between Abiotic vs. Biotic Media

Table 1 shows the strength and significance of monotonic relationships between PFAS in biotic vs. abiotic media based on Kendall's Tau correlation analysis. The results are summarized as follows:

- PFOSA shows generally stronger and more frequent correlations between biota vs. abiotic media pairs, followed by PFOS and then PFOA. PFDA and PFBA show statistically significant correlations in a limited set of the biota vs. abiotic media pairs that could be evaluated. A number of the PFDA and PFBA biota vs. abiotic media pairs could not be evaluated due to insufficient data.
- Only PFOSA shows strong correlation for FAV and snail vs. abiotic media.
- Correlations with surface water were generally stronger than other abiotic media for crayfish and forage fish. Statistically significant τ for PFOA, PFOS, and PFOSA in crayfish vs. surface water ranged from 0.4 to 0.6 and in crayfish vs. sediment ranged from 0.33 to 0.43. PFOA, PFOS, and PFOSA did not correlation for crayfish vs. pore water pair. For forage fish significant τ for PFOA, PFOS, and PFOSA ranged from 0.22 to 0.64 for surface water, 0.43 to 0.57 for pore water, and 0.31 to 0.43 for sediment.
- PFOS, PFOSA, and PFDA generally show moderate (τ = 0.4 - 0.6) to strong (τ > 0.6) correlations between higher TP biota and surface water, including forage, bottom, and predator fish.
- PFOA, PFOS, and PFOSA generally show moderate (τ = 0.4 - 0.6) correlations between amphibian and crayfish (with similar TPs) and surface water.

Table 1. Summary of Kendall's Tau Analysis of Select PFAS Concentrations in Biotic vs. Abiotic Media

Tissue Type	Abiotic Media[1]	PFOA			PFOS			PFOSA			PFDA			PFBA		
		n[2]	τ	p	n[2]	τ	p	n[2]	τ	p	n[2]	τ	p	n[2]	τ	p
FAV	Surface Water	19	-0.25	0.22	19	-0.04	0.83	15	0.71	0.00	19	-0.01	1.00	7	0.07	1.00
Snail	Sediment	6	-0.36	0.44	8	0.11	0.80	8	0.79	0.01	Insufficient Data			Insufficient Data		
	Pore Water	7	-0.62	0.09	7	-0.31	0.44	7	0.72	0.04	7	-0.62	0.09	Insufficient Data		
	Surface Water	8	0.00	1.00	8	-0.11	0.87	8	0.65	0.07	8	-0.33	0.40	Insufficient Data		
Amphibian	Sediment	10	0.46	0.09	18	0.21	0.24	9	0.40	0.17	Insufficient Data			Insufficient Data		
	Pore Water	10	0.60	0.02	18	0.21	0.25	13	0.67	0.00	12	0.05	0.89	13	-0.27	0.24
	Surface Water	10	0.55	0.07	18	0.55	0.00	13	0.55	0.02	18	0.04	0.87	13	-0.02	1.00
Crayfish	Sediment	34	0.15	0.23	35	0.33	0.01	23	0.43	0.01	Insufficient Data			7	0.72	0.06
	Pore Water	26	0.08	0.61	26	0.20	0.18	16	0.05	0.82	16	-0.17	0.41	26	0.46	0.00
	Surface Water	40	0.59	0.00	40	0.40	0.00	40	0.60	0.00	40	-0.25	0.04	40	0.54	0.00
Forage Fish	Sediment	23	0.31	0.05	25	0.32	0.03	16	0.42	0.03	6	-0.45	0.32	Insufficient Data		
	Pore Water	17	0.48	0.01	19	0.57	0.00	13	0.43	0.05	8	0.11	0.80	16	0.27	0.18
	Surface Water	48	0.22	0.04	51	0.64	0.00	50	0.62	0.00	51	0.38	0.00	40	-0.08	0.54
Predator Fish	Sediment	Insufficient Data			6	0.36	0.44	Insufficient Data			Insufficient Data			Insufficient Data		
	Pore Water	Insufficient Data			Insufficient Data			Insufficient Data			Insufficient Data			Insufficient Data		
	Surface Water	19	-0.01	1.00	25	0.44	0.01	25	0.79	0.00	25	0.33	0.04	6	-0.08	1.00
Bottom Fish	Sediment	Insufficient Data			5	0.20	0.81	5	0.00	1.00	Insufficient Data			Insufficient Data		
	Pore Water	Insufficient Data			Insufficient Data			Insufficient Data			Insufficient Data			Insufficient Data		
	Surface Water	Insufficient Data			5	0.89	0.07	5	0.67	0.19	5	0.89	0.07	5	0.45	0.43

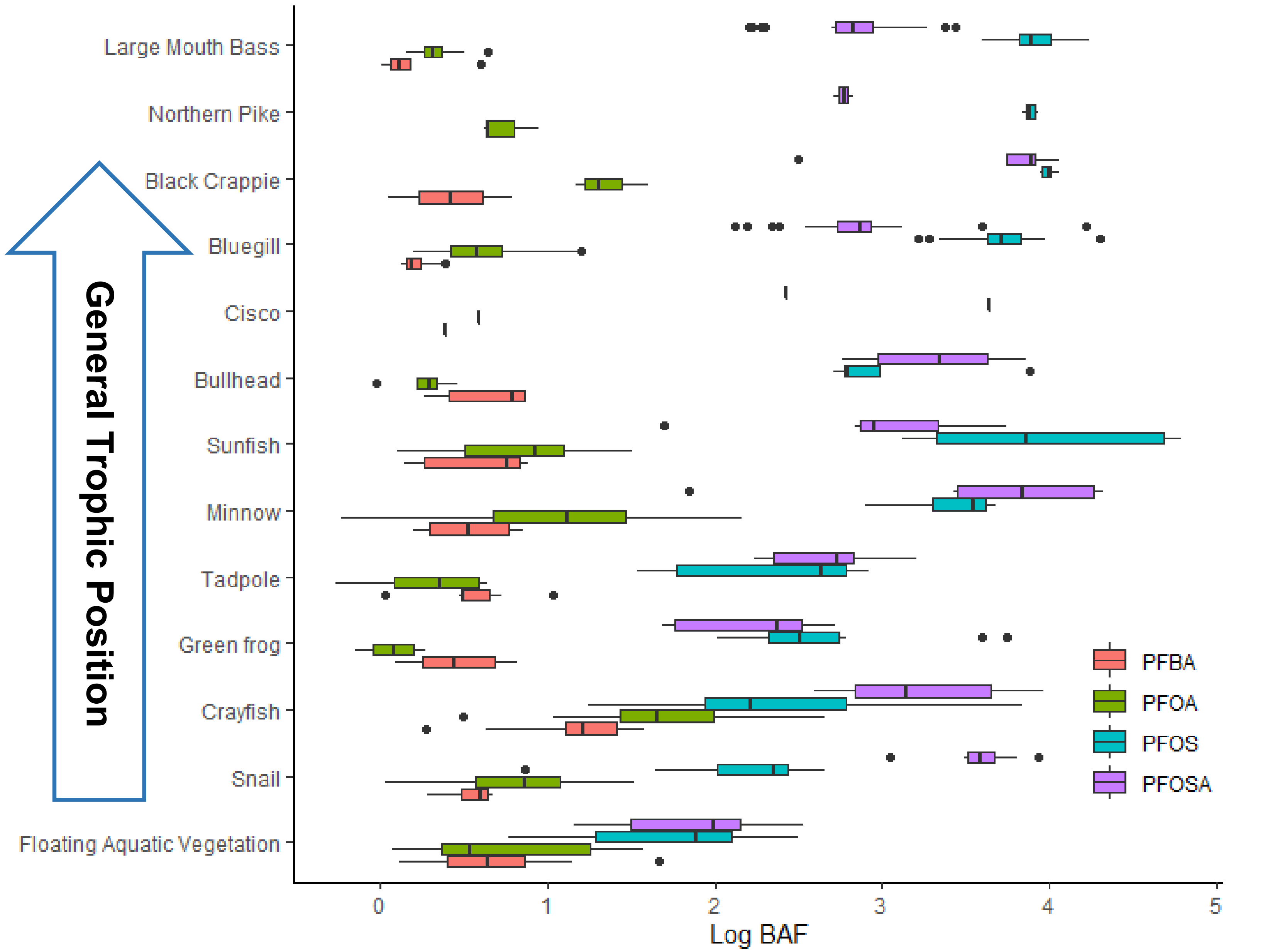
NOTES:
FAV - floating aquatic vegetation; n - number of data points; τ - Kendall correlation coefficient; p - significance level; Insufficient Data - less than 5 detected paired samples of biotic and abiotic media.
Analysis was conducted using detected paired samples of biotic and abiotic media.
[1] Geomean of surface water data in each sub-area between 2019 and 2021 (for pairing with plant datasets) and between 2019 and 2020 (for pairing with the rest of the tissue datasets).
[2] Sample size is the number of detected paired samples.
Significant correlation using a significance level of 0.05 ($p \leq 0.05$)
Significant correlation using a significance level of 0.1 ($p \leq 0.1$)

Bioaccumulation Factors (BAFs)

Observations on the BAFs for various species (see Figure 4) are summarized as follows:

- Bioaccumulation potential follows the general order (high to low): PFOS (long chain sulfonic acid) > PFOSA (long chain sulfonamide) > PFOA (long chain PFCA) > PFBA (short chain PFCA)
- Differences in BAFs between PFBA/PFOA vs. PFOSA/PFOS and PFOSA vs. PFOS increase among the species with increasing trophic level, with BAFs for predatory fish species (high TP) having the greatest differences among the PFAS compounds.

Figure 4. **Site-Specific Bioaccumulation Factors (BAFs) for Sampled Species and Select PFAS**



NOTES:
BAF - Bioaccumulation Factor
BAF = Concentrations in biota (µg/kg wet weight) / concentrations in surface water (µg/L) where, concentrations in surface water = area-specific geometric mean concentrations (unfiltered)

Site-Wide Trophic Magnification

Table 2 shows the results of the Kendall's Tau correlation to determine site-wide Trophic Magnification Factors (TMFs) following the approach by Miranda et al. (2021). Select graphical examples of the regressions are shown in Figure 5. Observations on the patterns in site-wide TMFs are summarized as follows:

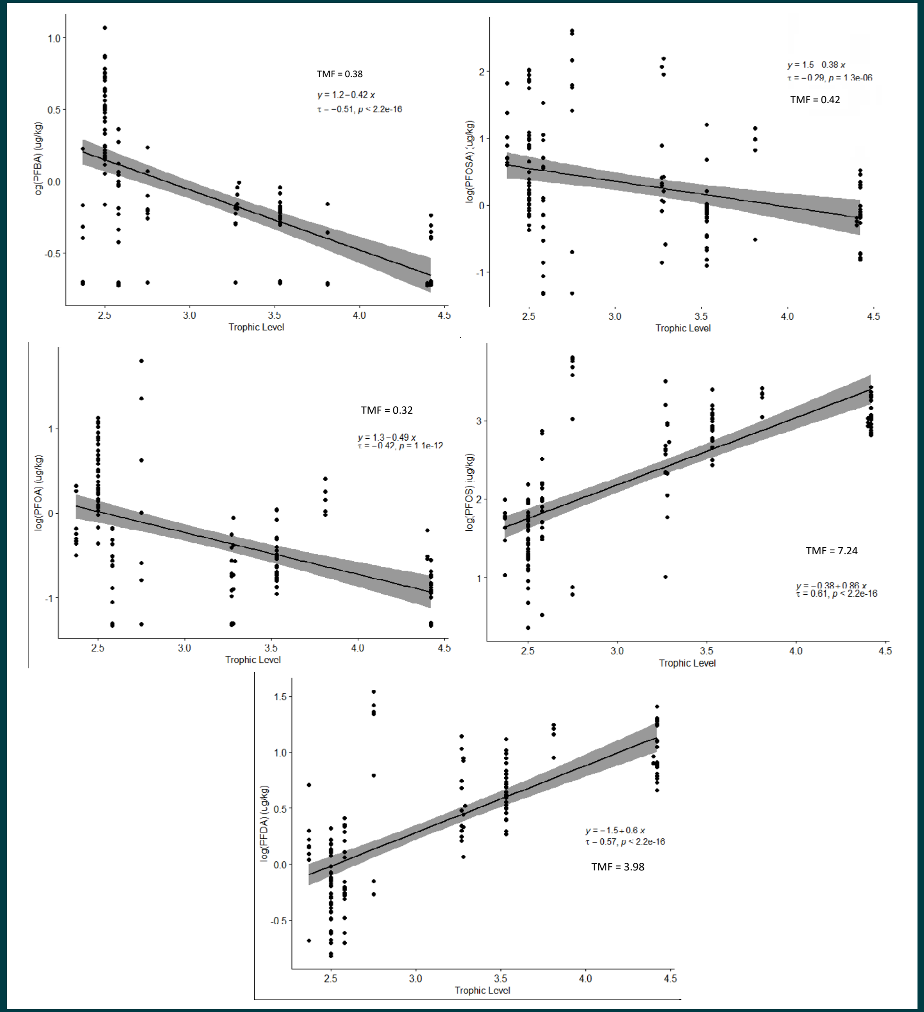
- Correlations are significant ($p < 0.05$) for all presented PFAS, except N-EtFOSSA; however, not all PFAS biomagnify, e.g., PFBA, PFOA, and PFOSA with TMF < 1.
- Site-wide TMFs for specific PFAS are similar to the mean and within the range reported for freshwater food webs (Miranda et al., 2022); the highest TMF in this study was calculated for PFOS (7.24), which is higher than the literature-reported mean (3.9) but within the range (0.8 to 9.9).
- Among PFCAs shown, the general and unimodal trend with peak TMF for PFDA (with carbon chain length of 10) is consistent with that reported in the literature.
- Two sulfonic acids (PFHpS and PFOS) also appear to show TMF dependency on carbon chain length.
- Only PFOS (a long chain sulfonic acid) shows bioaccumulation potential (TMF > 1) among PFAS of the same carbon chain length but different functional groups (PFOA, PFOS, and PFOSA).

Table 2. Results of Kendall's Tau Correlations of PFAS Concentrations (Logarithm) vs. Trophic Position (TP)

PFAS		FOD (%)	Detected Concentration (µg/kg)			τ	p	Trophic Magnification Factor (TMF)	
Compounds	CCL		Minimum	Mean	Maximum			This Study	Miranda et al. (2022)[2]
Carboxylic Acids									
PFBA	4	74	0.38	1.85	11.7	**-0.51**	0.00	**0.38**	0.8 (0.4 - 1.3)
PFOA	8	88	0.094	1.99	63.4	**-0.42**	0.00	**0.32**	1.3 (0.4 - 3.6)
PFDA	10	100	0.151	5.19	34.8	**0.57**	0.00	**3.98**	4 (0.8- 11)
PFUnA	11	100	0.116	1.02	5.19	**0.51**	0.00	**2.29**	3.4 (0.5 - 7.2)
PFDoA	12	96	0.096	0.68	6.44	**0.18**	0.00	**1.29**	2.1 (0.3 - 3.7)
PFTeDA	14	72	0.096	0.27	1.71	**0.14**	0.02	**1.25**	1.6 (0.2- 2.9)
Sulfonic Acids									
PFHpS	7	65	0.094	0.75	39.6	**0.45**	0.00	**2.82**	2.9 (0.7 - 8.3)
PFOS	8	100	2.3	764	6350	**0.61**	0.00	**7.24**	3.9 (0.8 - 9.9)[3]
Others									
PFOSA	8	96	0.094	16.7	405	**-0.29**	0.00	**0.42**	1.1 (0.5 - 2.5)
N-EtFOSAA	12	75	0.092	1.65	38	-0.02	0.74	0.79	1.5 (0.6 - 2.3)

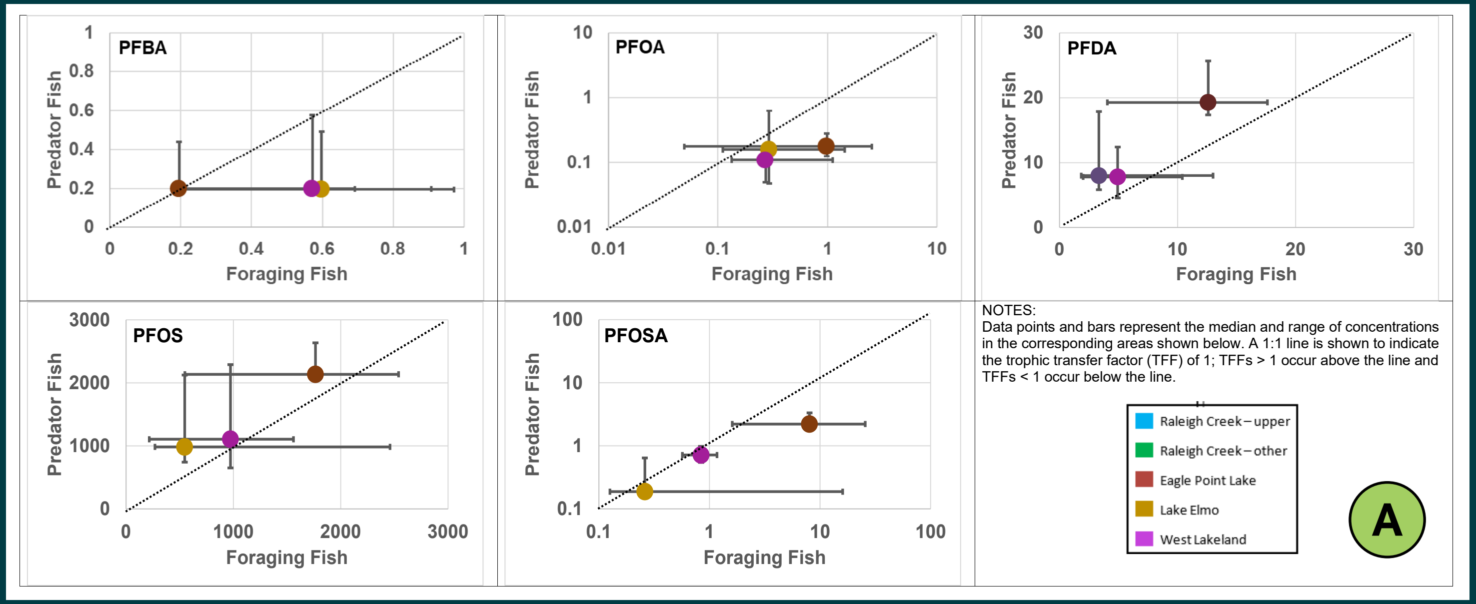
NOTES:
FOD - Frequency of detection (%)
CCL - Carbon chain length
τ - Kendall's Tau correlation coefficient
p - statistical significance
NA = Not available
TMF calculated as 10^{slope} [see Figure 5 and Miranda et al. (2021)]
τ and TMF values in bold indicate significant correlations ($p < 0.05$).
[1] Trophic position (TP) of the species sampled was not specifically determined in this study. Species TPs were assigned based on the estimated trophic level designated for each species or similar species by Burkhard (2021).
[2] Mean and Range (in parenthesis) of TMFs for freshwater food webs as reported by Miranda et al. (2022).
[3] For linear PFOS.

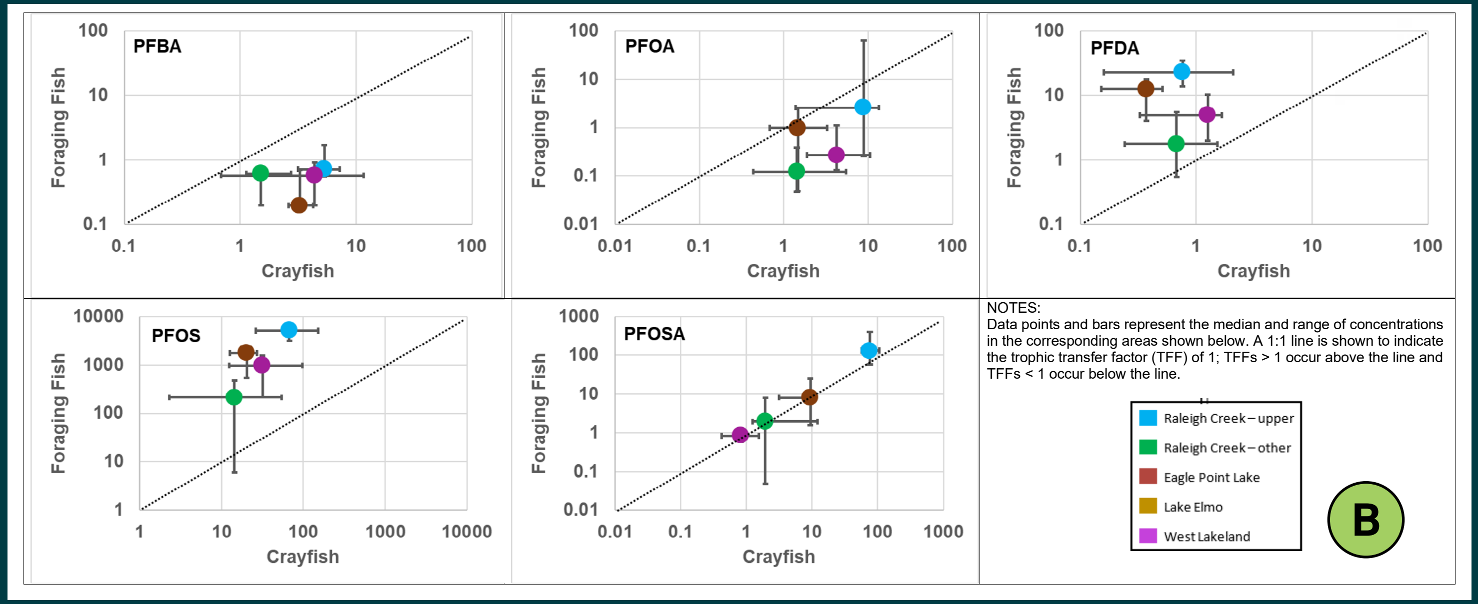
Figure 5. Kendall's Tau Correlations of PFAS Concentrations (Logarithm) vs. Trophic Position (TP) for Select PFAS

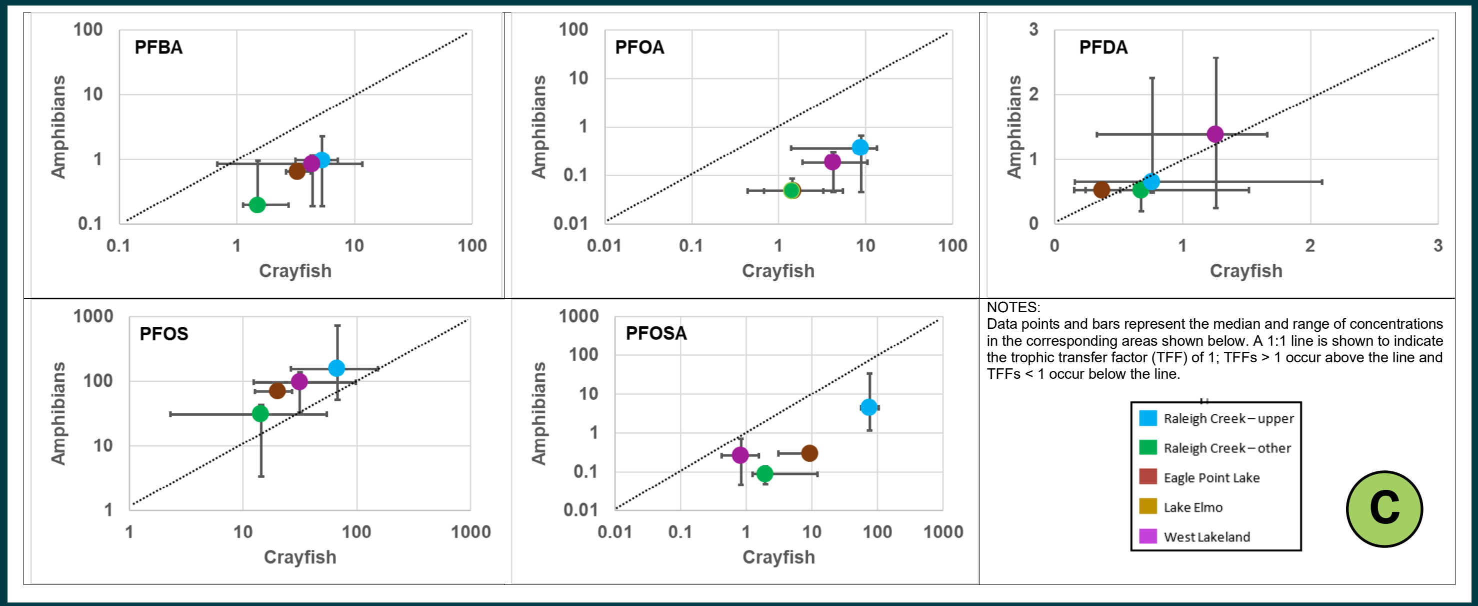


Area-Specific Trophic Transfer

Figure 6. Trophic Transfer Between Biota Pairs: A) Predator Fish vs. Foraging Fish, B) Foraging Fish vs. Crayfish, and C) Amphibians vs. Crayfish







Figures 6A, B, and D compare the trends in detected PFAS concentrations in specific areas in select organisms at different TPs as estimated for same or similar species from Burkhard (2021): predator fish (TP = 4.2), forage fish (TP = 2.75 to 3.81), amphibians (TP = 2.58) and crayfish (TP = 2.5). The ratio of concentrations in different biota provides a measure of trophic transfer factor (TTF) between them (and their TPs).

Observations on the spatial patterns in Figures 6A, B, and C are summarized as follows:

- For the PFCAs, TTFs generally increase between all three pairs of biota, with TFF < 1 (i.e., below the 1:1 line) for PFBA to TFF ≥ 1 for PFDA.
- For PFAS with the same chain length and different functional groups, the TFFs < 1 for PFOA, the TFFs ≤ 1 for PFOSA, and the TFFs > 1 for PFOS.
- In some cases, concentrations in higher and lower TP biota pairs vary consistently across sub-areas reflecting similar TFFs despite proximity to sources and release history. PFOSA in foraging fish vs. crayfish and PFOS in amphibians vs. crayfish exemplify this trend. However, the same biota pairs indicate substantially different TFFs for other PFAS across the different areas (e.g., PFDA in foraging fish vs. crayfish), potentially reflecting differences in PFAS accumulation in the sub-areas.

Overall Findings

Based on the observations from the various evaluations summarized in this study, the following findings are supported:

- PFOS dominates the speciation and distribution in abiotic and biotic media in Project 1007 waterways and shows the greatest potential for site-wide bioaccumulation and trophic magnification; estimated TMF = 7.24 for PFOS is higher than the mean (3.9) and at the upper end of the range (0.8 to 9.9) reported in the literature and may reflect site-specificity, methodological differences, or other factors (such as precursors).
- Concentrations in abiotic media in Project 1007 waterways generally decrease further from the source areas for long chain PFAS, but not necessarily for short chain PFAS (PFBA), reflecting the PFAS release history, area hydrogeology, and compound-specific geochemical fate and transport factors. Biotic media shows a similar decreasing trend with distance from the source areas reflecting the trend in the abiotic media; however, the decreases with distance are not as pronounced for short chain PFAS as the long chain PFAS.
- Estimated site-wide TMFs are similar to the mean and within the range of TMFs reported in the literature for aquatic food webs in freshwater systems; some differences in the trophic transfers among the sub-areas were observed for specific PFAS (e.g., PFDA in foraging fish vs. crayfish pair); thus, localized differences in trophic structure may be of importance in understanding biomagnification of specific PFAS.
- Estimated site-wide TMFs for PFCAs indicate carbon chain length dependency, with a peak TMF observed for PFDA and decreasing TMFs as chain length deviates further from that of PFDA in either direction; this trend in TMFs is consistent with those reported in the literature, and is often attributed to interactions between greater uptake and accumulation potential for longer chain PFAS but progressively lower bioavailability and size limitations of cellular uptake beyond a certain size of PFAS molecules.
- PFAS concentrations in foam relative to surface water are enriched by approximately three orders of magnitude, reflecting their surfactant properties and may have implications for wildlife exposure via incidental exposures specifically to foam.

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CONTACT:

Sagar Thakali, Ph.D.
Principal Risk Assessor
D 1-610-234-4903
sagar.thakali@aecom.com

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