

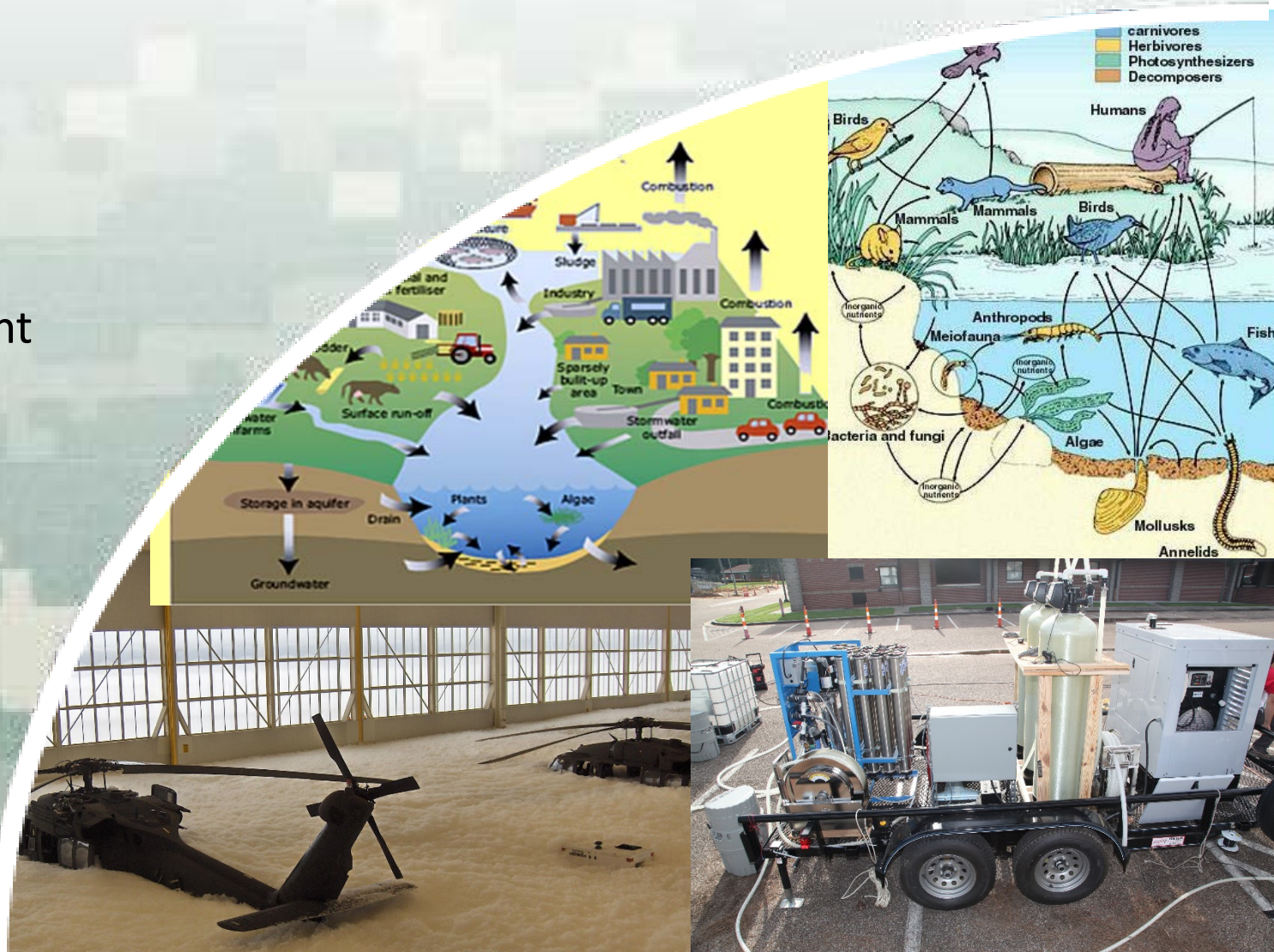
PFAS Overview

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PFAS Overview

- Use of AFFF firefighting foams, DoD wide, since early 70's.
- Significant liability to DoD most recent estimate >\$2B
- Army just issued guidance (September)
 - ▶ Investigation and inventory of sites (storage, training locations, hangar facilities, plating facilities, crash sites, landfills, wastewater treatment plants, etc.) focused on human health-based exposures.
 - ▶ Drinking water assessments at all installations
 - ▶ Preliminary Assessment (PA) – Site Inspection (SI) – Remedial Investigation (RI) (RIs focused where human drinking water exposure confirmed).
 - ▶ Prioritization “worst first” approach



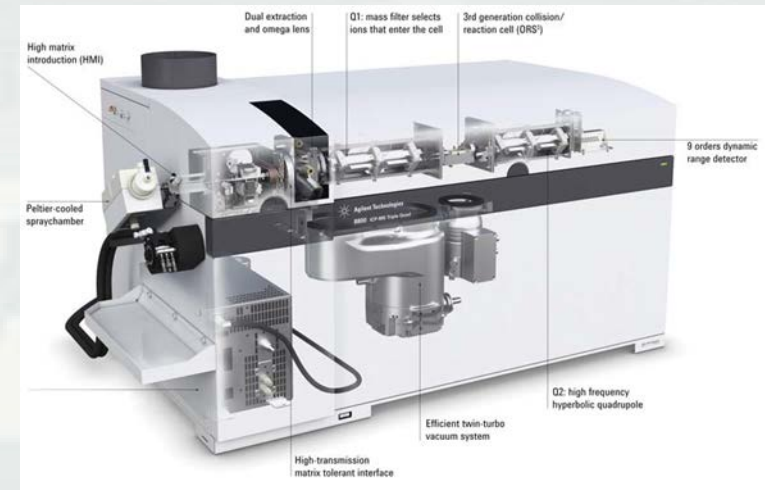
PFAS Overview

- Currently, 126 Army installations impacted with several reliant on alt water sources
- Corps providing technical support (Airforce and Army Installations) – primarily focused on remediation
- Unique Challenges
 - ▶ Highly stable, hydrophobic and lipophobic (unlike traditional ECOC's)
 - ▶ 3000 compounds
 - ▶ Global distribution (including sources other than AFFF) (NHANES 2013-2014 detected PFOS, PFOA >99% of indiv.)
 - ▶ Extremely low health advisory levels (70ppt) potential to go lower (ATSDR, states)
 - ▶ Analytical methods currently only for water, other environmental media in development



PFAS Overview

- DoD in reactive/response mode
 - ▶ identification and remediation of drinking water and groundwater contamination with PFOS/PFOA focus;
 - ▶ R&D emphasis
 - analytical methods (Triple Quad MS, water)
 - remediation technology (GAC → single use resins; ex situ vs in situ)
 - ▶ additional PFASs under evaluation (PFHxAs, and some of the shorter chain compounds);
 - ▶ just underway:
 - Pathways other than drinking water exposure (e.g., sediment, soil, food);
 - Eco (uptake, transfer, and effects)



Knowledge Gaps - Analytical

- Existing methods primarily for aqueous matrices
 - ▶ USEPA 537 is only approved for drinking water
 - ▶ Modifications to this method to complex water matrices yield unknown data quality and potential analytical shortfalls
- Relatively short list of target analytes monitored
 - ▶ USEPA 537 targets 14 compounds
 - ▶ Thousands of potential compounds of interest (e.g. precursors, degradation products, branched structures, etc.)
- Application to solid matrices is challenging
 - ▶ Soils, sediments, and tissues will each present extraction and analysis challenges
 - ▶ Method development, comparison, and validation studies are required

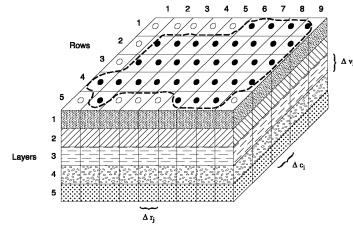


Knowledge Gaps- Fate & Transport



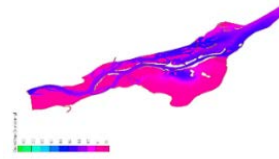
+

Groundwater



+

Hydrodynamics



For the vast majority of PFAS compounds we do not know:

1) BioGeoChemical properties

- PFAS degradation pathways
- Degradation rates

These properties are needed to determine how the PFAS waste mixtures evolve over time.

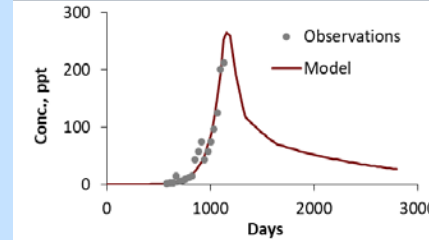
Fate mechanisms



Bench Scale



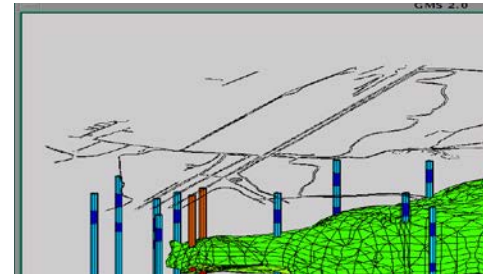
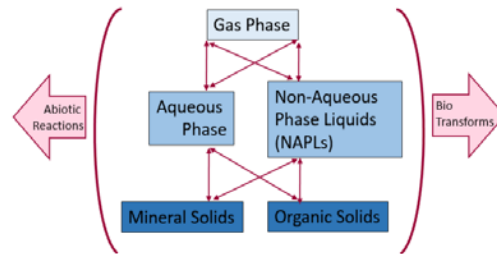
Parameterization



Multimedia Site concept →

Integrated Environmental Processes →

Fate and Transport Modeling



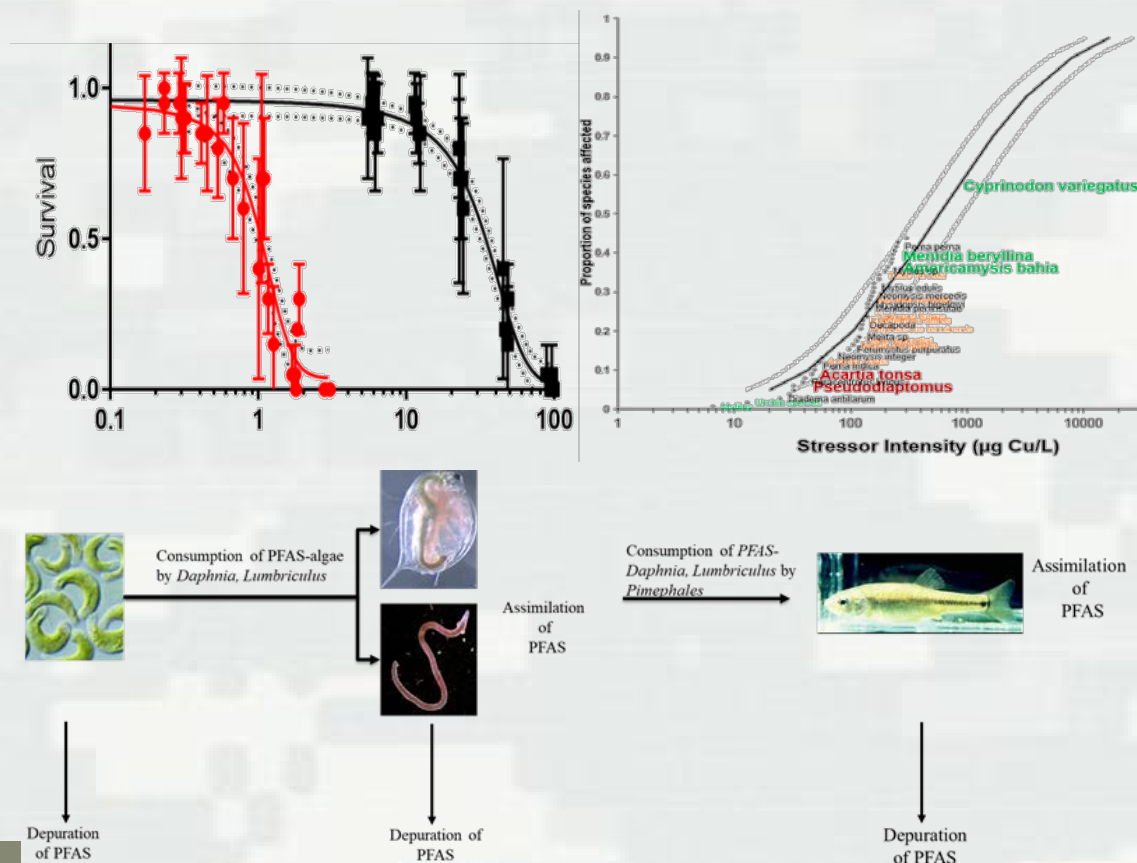
2) Fate determining properties for PFAS and degradation products

- Solubility
- Henry's constant
- Solid partitioning constants

These properties are needed to assess interactions with soils, dissolved solids, and non-aqueous liquids as well as transformations between phases.

Knowledge Gaps – Uptake, Trophic Transfer, Effects

- Relative bioavailability of different PFAS compounds
- Data availability to determine more appropriate protective threshold levels
- Species sensitivity distributions
- Partitioning between different
 - ▶ Trophic levels
 - ▶ Organism tissue compartments
- Appropriate parameters to update predictive models for PFASs



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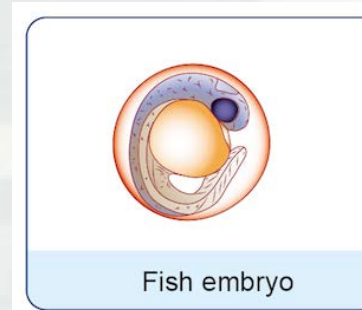
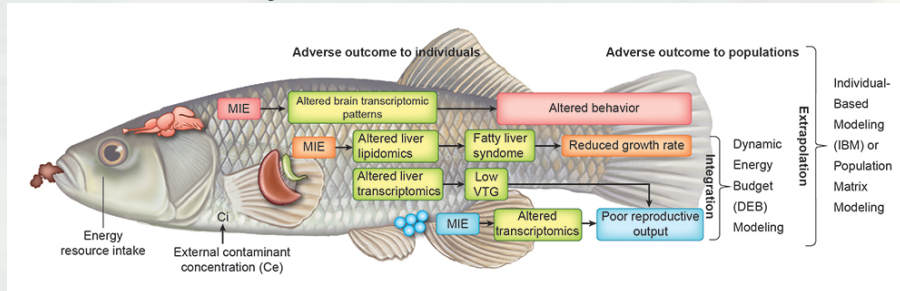


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Knowledge Gaps – Mode of Action / Adverse Outcome

- Mechanism(s) of action
- Adverse Outcome Pathways (Networks)
- Species sensitivity
- Life stage sensitivity
- Data to inform predictive computational models
- Accurate docking/binding models to predict toxicity



$$\frac{dLs}{dt} = N \cdot K_1 - (d_1 + r) \cdot Ls + \delta_1$$

$$\frac{dLux}{dt} = \left(\frac{K_2}{1 + A \cdot Ls^2} \right) \cdot N - (d_2 + r) \cdot Lux + \delta_2$$

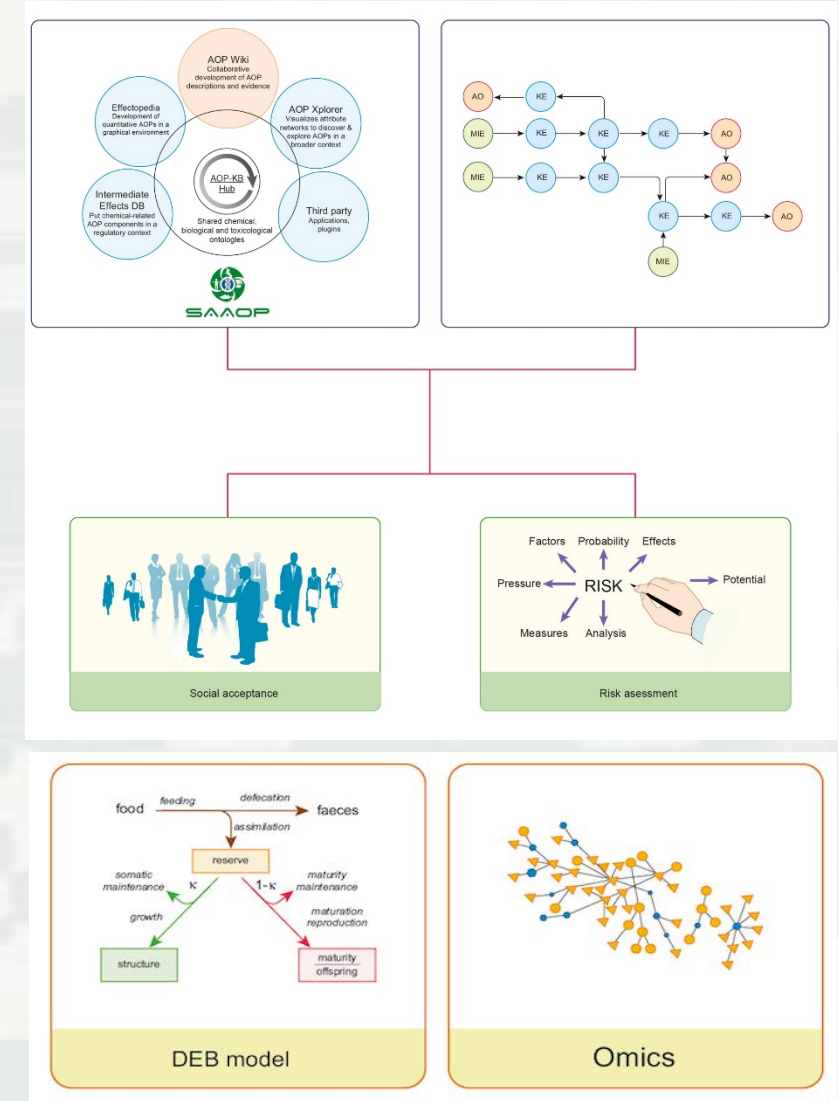
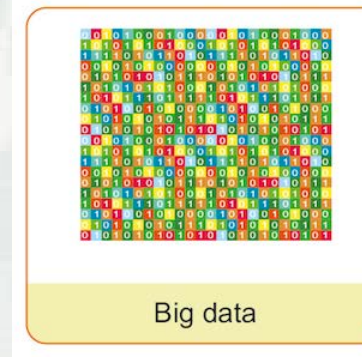
$$Z = Z_1 + Z_2$$

$$Z_1 = K_3 \cdot Lux$$

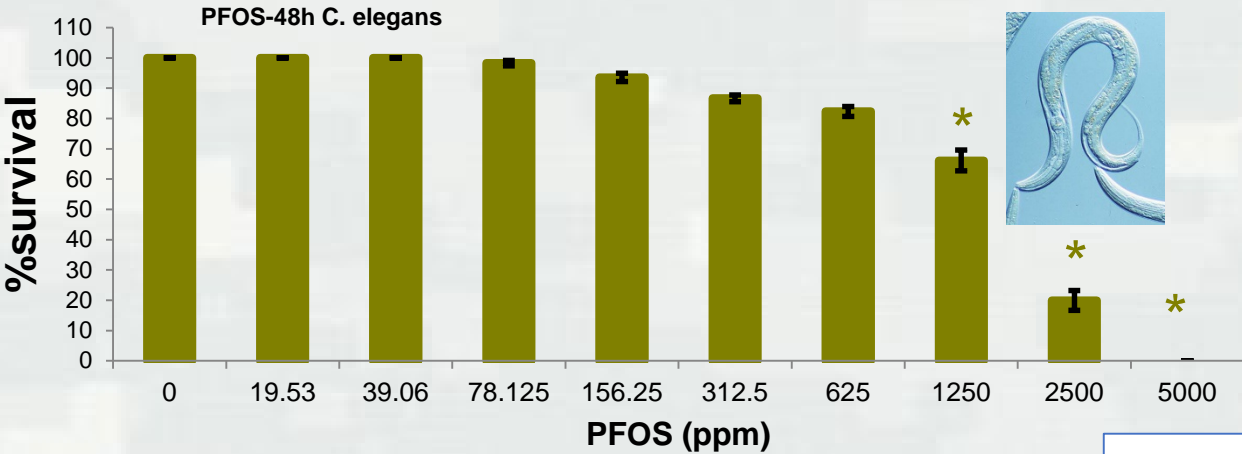
$$Z_2 = \int_0^{\infty} \int_0^{\infty} Z \, ds$$

$$\frac{dLs1}{dt} = \left(1 - \frac{Ls}{K_5} \right) \cdot \left(1 - \frac{Z}{K_6} \right)$$

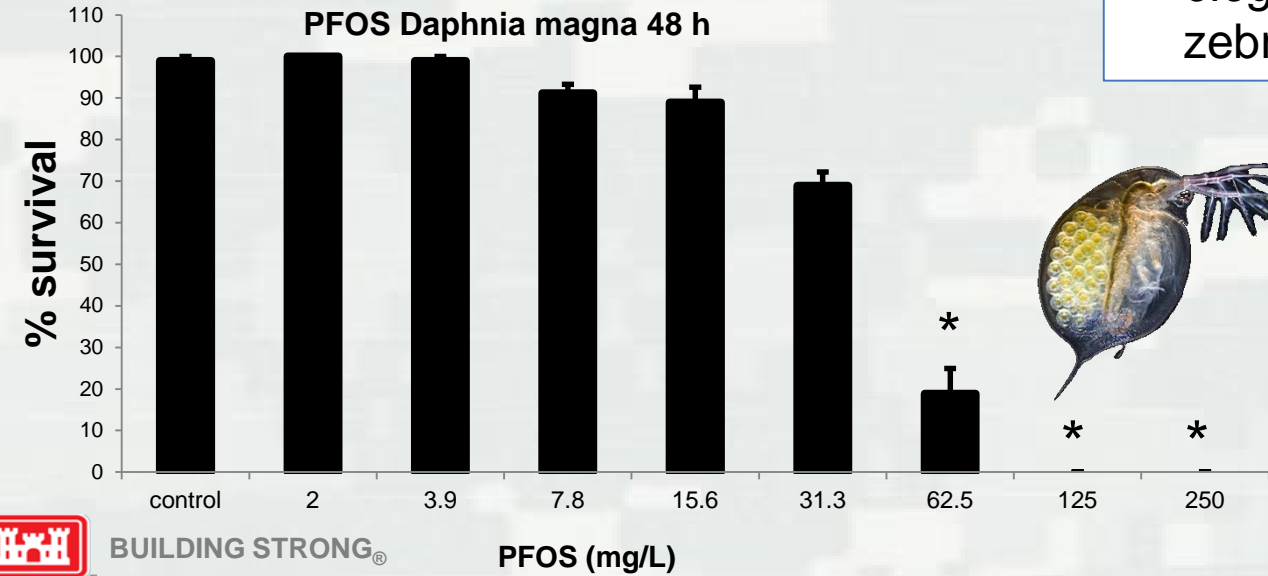
Mathematical model



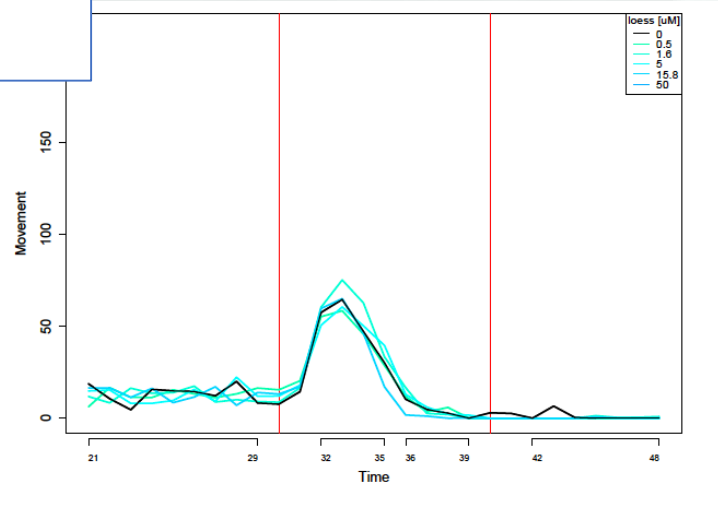
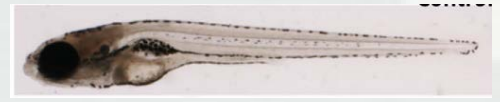
Ongoing Work – Mode of Action / Adverse Outcome



Genomic samples: 78.125, 39.06, 19.53, 9.765, 4.88 mg/L



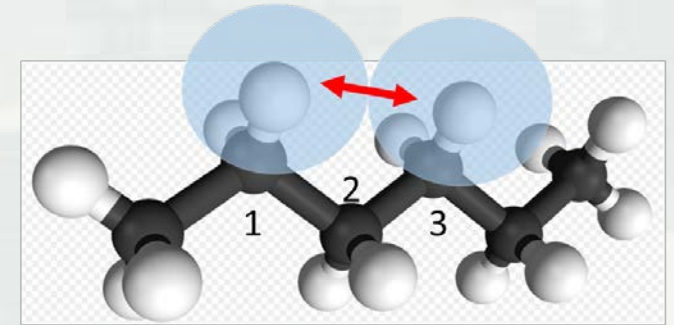
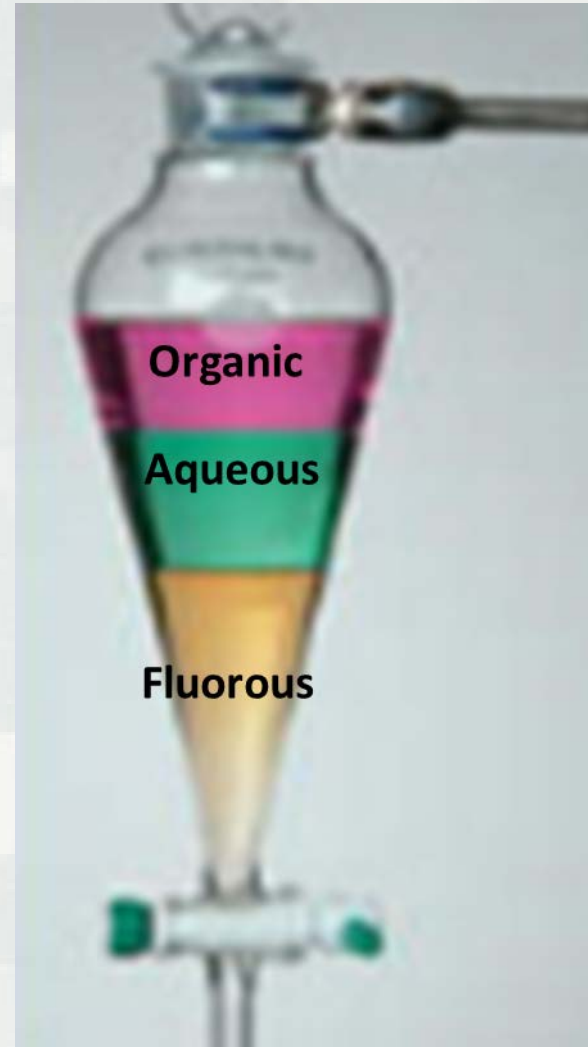
- Apical endpoints, (*C. elegans*, *Daphnia magna*, zebrafish embryo)



Knowledge Gaps – Remediation / Treatment

Wide range of PFAS chain lengths, configurations, and precursors

- Myriad of chemical configurations
- Diverse interactions with environment
- (GAC) filtration for short-chain PFAS
- (RO) membranes for short-chain PFAS
- Ion exchange resins show promise but require a good deal of further study
- Electrocatalytic Degradation possible but scalability and deleterious by-products are a concern
- Physically hydrophobic, oleophobic, and lipophobic - tends to associate with proteins



1,3 repulsions force the F atoms out of linearity



Implications

- Issues are already being raised in Great Lakes Region (Michigan)

Re: beneficial use and in lake disposal

- If you have airports, military installations, refineries, or fire training areas – could be coming to a theater near you.
- Papers have been published showing presence in SF Bay seds
- Some indication that PFAS associates with sediments in marine estuarine environments more so than in FW systems.

Next Steps

- Development and validation of analytical methodologies for range of environmental media other than drinking water
- Better understanding of mode of action and potential human health risks.
- Improved understanding of fate, transport, uptake, and transfer/biomag. mechanisms
- Rationale/approach for addressing mixtures (exposure, uptake, and toxicity)
- Cost effective remedial strategies, regenerative resins and cost effective destructive technologies, *in situ* as opposed to *ex situ* methods (especially for soils/sediments)
- Framework for proactively identifying and addressing ECOCs (avoid reactive science and policy decisions)