# Soil Invertebrate and Terrestrial Plant Tissue Uptake of PFAS at a Former Firefighter Training Area

## Comparison of Site Specific and Literature Bioconcentration Factors and Implications for Site Specific Target Level Derivation


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# Outline

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- Sample Collection Method
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- Considerations for Site Specific Target Level Derivation
- References

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# Background

## Site

- Three former firefighting training areas (FFTAs) are present at the Site, two of which were used for hot drills
- The operational period was mid 1950’s to early 1990’s
- AFFF containing per- and polyfluoroalkyl substances (PFAS) was used during fire fighting training exercises
- Soil, groundwater, surface water and sediment at the Site are impacted to varying degrees by PFAS
- PFAS is present in a number of terrestrial and aquatic biological media at the Site

# Background

- The following PFAS have been characterized at the Site in various media:

| PFCA | PFSA |
|---|---|
| Perfluorobutanoic acid (PFBA) | Perfluorobutane sulfonic acid (PFBS) |
| Perfluoropentanoic acid (PFPeA) | Perfluorohexane sulfonic acid (PFHxS) |
| Perfluorohexanoic acid (PFHxA) | Perfluorooctane sulfonic acid (PFOS) |
| Perfluoroheptanoic acid (PFHpA) | Perfluorooctane sulfonamide (PFOSA) |
| Perfluorooctanoic acid (PFOA) | |
| Perfluorononanoic acid (PFNA) | |
| Perfluorodecanoic acid (PFDA) | |
| Perfluoroundecanoic acid (PFUnA) | |
| Perfluorododecanoic acid (PFDoA or PFDoDA) | |

- The Site data discussed is limited to co-located tissue-soil samples which represent a small subset of all samples collected at the Site

# Study Objectives

Reduce ecological risk assessment modelling uncertainty associated with PFAS uptake from soil to food items

Identify the bioaccumulation dynamics of specific PFAS in soil invertebrates and terrestrial plants

- Correlate soil PFAS concentrations with tissue PFAS concentrations to develop a simple predictive uptake model
  - Necessary to identify site-wide tissue exposure point concentrations to assist in ecological risk assessment modelling
  - Kow typically used as a proxy for tissue uptake by organic chemicals. It is well established that an octonol-water based partition relationship (Kow) is not appropriate for PFAS which limits predictive modelling, therefore Site specific data is preferred

# Sample Collection Method

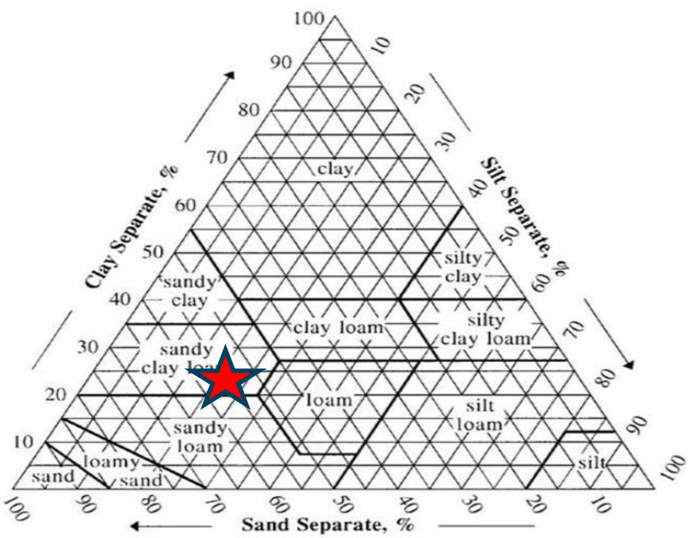
- Each soil invertebrate, terrestrial plant and soil sample were collected from common sampling plots, typically in an area of 1 $m^2$
  - All samples were collected in the root zone at a depth less than 0.3 mbgs
- Soil invertebrates were allowed to depurate as much as possible before rinsing and storage on dry ice in polyethylene containers
  - Soil invertebrates consisted of earthworms, although in a few cases, due to limited sample recovery, White grub (June beetle) were included in samples containing earthworms
- Terrestrial plant samples were rinsed prior to storage on dry ice in polyethylene containers
  - Samples consisted mostly of grasses and were composed only of above grade portions of the plants
- Typical quality assurance and control procedures established for sampling involving PFAS were adhered to
- The analytical laboratory performed all tissue homogenization

# Soil and Tissue PFAS Chemistry

## Soil

7.61 to 1168 ng/g (DW) ΣPFAS

- 1.03 to 5.73% organic carbon
- Silty fine sand to fine silty sand (USDA sandy clay loam)




## Tissue

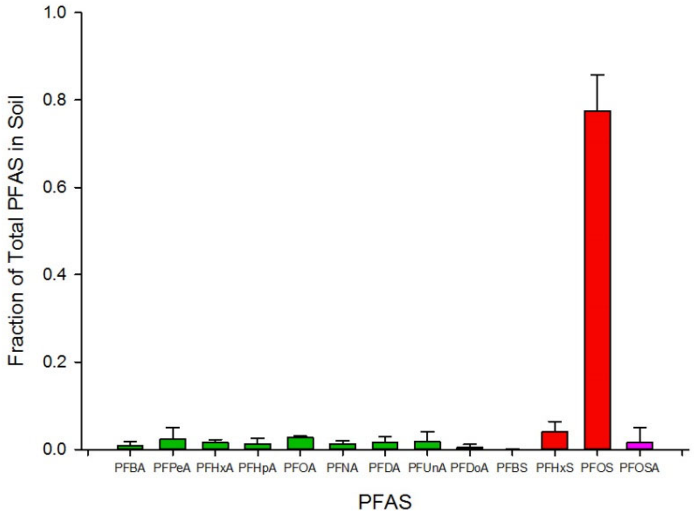
Soil invertebrates = 246 to 39805 ng/g (WW) ΣPFAS

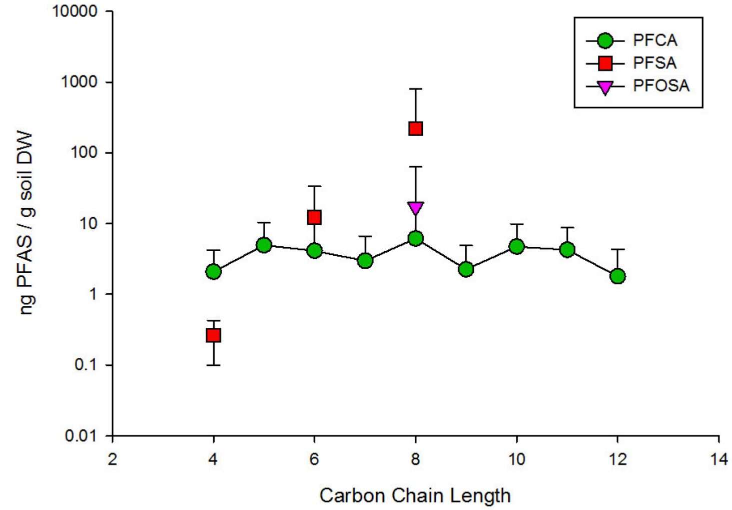
- 66% to 81% moisture content

Terrestrial plants = 2.3 to 2648 ng/g (WW) ΣPFAS

- 66% to 86% moisture content

# Soil Chemistry



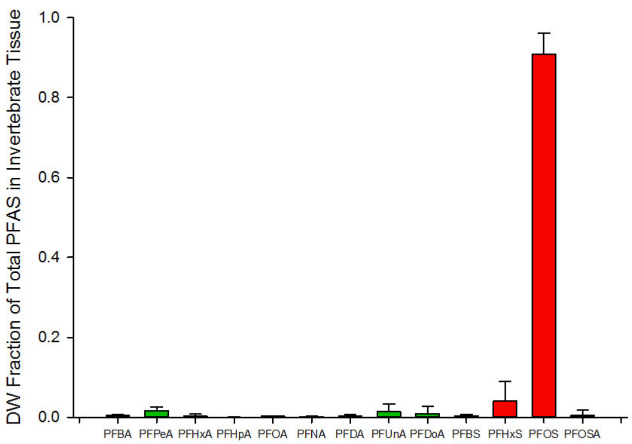

Soil PFAS chemistry dominated by PFOS (>68% of analyzed PFAS, typically 75% to 85%)

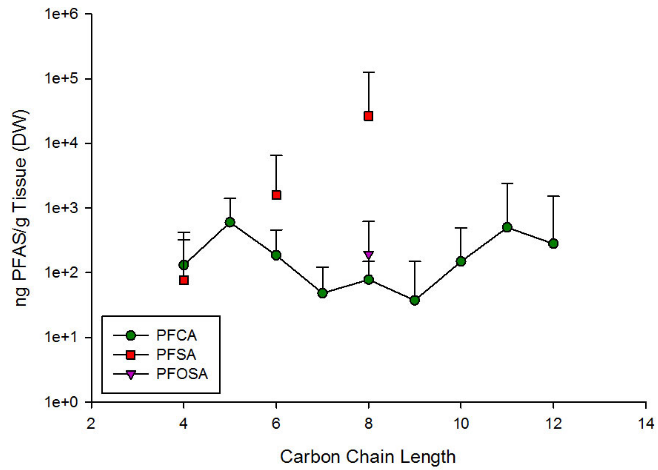
- PFSA consists of >72% of PFAS present in the soil samples
- Composition is generally compatible with a legacy AFFF source[2, 3, 4]



DW = Dry Weight basis

# Soil Invertebrate Tissue Chemistry




Site tissue PFAS chemistry dominated by PFOS (67% to 96% of analyzed PFAS)

- PFCA comprise <16% of tissue PFAS
- Majority of PFAS present are $C_{\geq 11}$ (PFCA) or $C_{\geq 8}$ (PFSA)
- Minor concentration variation for PFCA over a $C_4$ to $C_{12}$ range while PFSA exhibit significant uptake variation with increasing carbon chain length
- PFAS distribution generally similar to literature based observations

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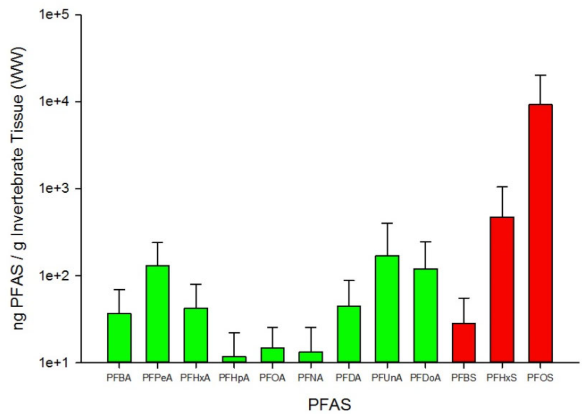
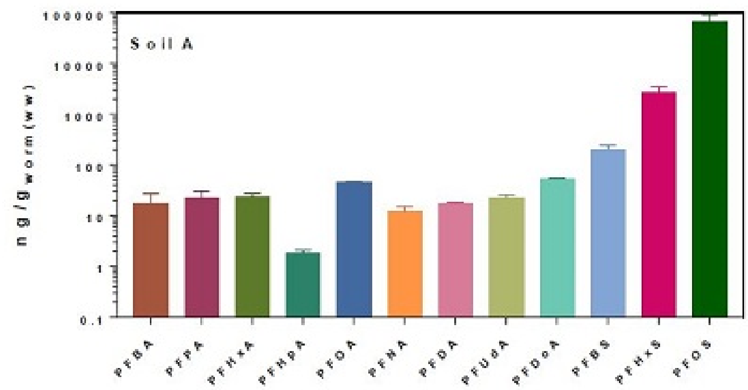
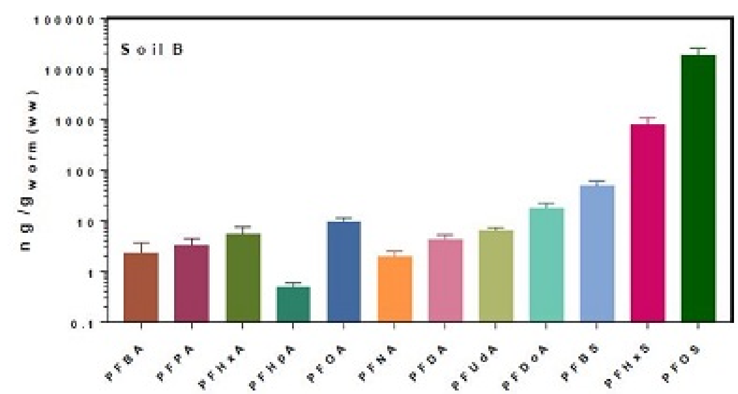
# Invertebrate Tissue Literature Comparison

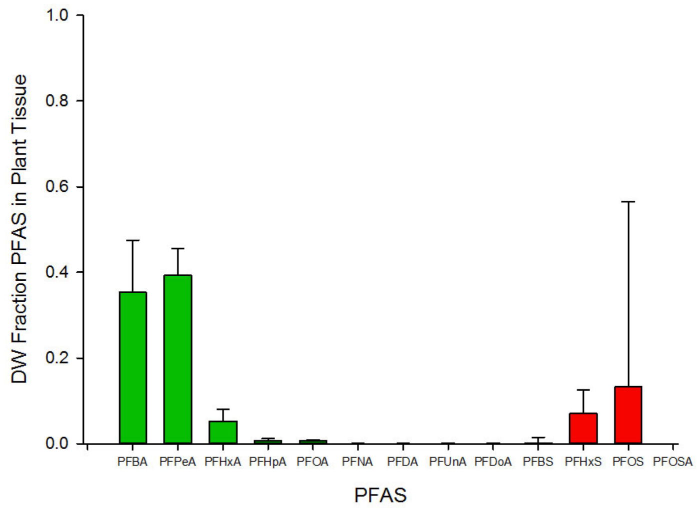


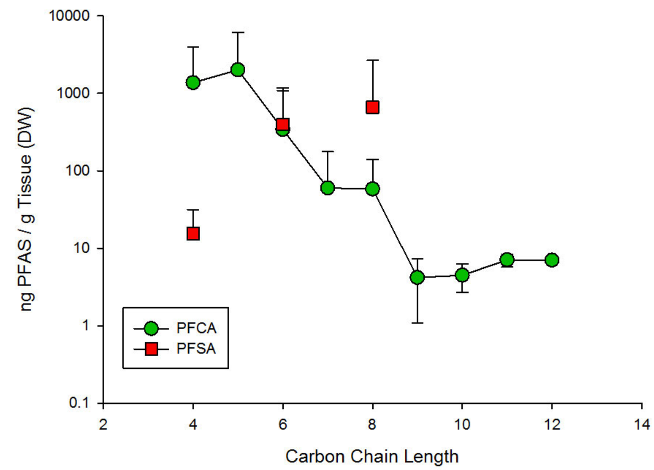




- Generally minor overall PFCA concentration variation relative to PFSA
- Dominant PFAS are PFSA $C_6$ (PFHxS) and $C_8$ (PFOS)
- Lowest concentration PFAS consists of PFHpA

# Terrestrial Plant Tissue Chemistry




Site tissue PFAS chemistry dominated by short chain PFCA (>42% of the samples are comprised of $C_4 + C_5$) and long chain PFSA

› PFAS distribution in tissue is similar to that identified in the literature

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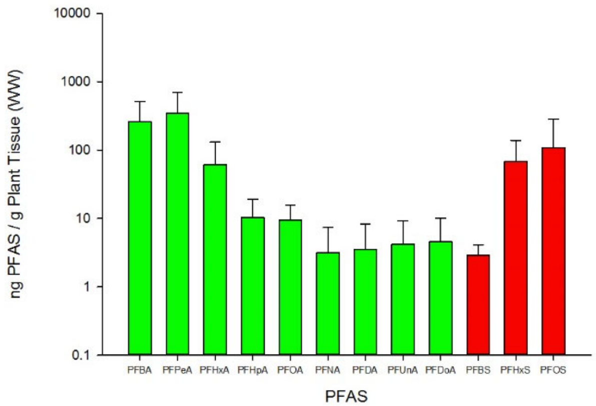
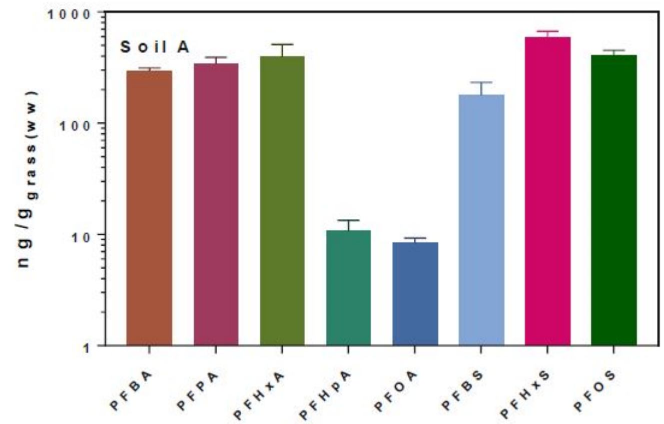
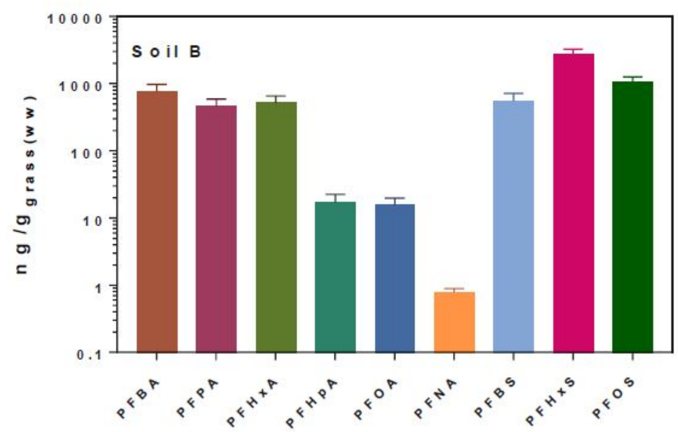
# Plant Tissue Literature Comparison




- Relatively short chain PFCA uptake to plant tissue to a higher degree relative to longer chain PFCA
- Inverse uptake relationship between long chain PFCA and PFSA



# PFAS Uptake Factor Identification

Soil to biota uptake equations can be described as simple ratios of the chemical concentrations in soil and tissues, or can be described through regression equation modeling[23]. The simple ratio bioconcentration/accumulation factor represents the following:

$$BCF or BAF = \frac{C_{tissue,DW}}{C_{soil,DW}}$$

The process for identifying Site specific PFAS uptake relationships was as follows:

- Tissue concentration data were converted to dry weight basis concentrations
  - Conversion is necessary to remove PFAS concentration variability imposed by differences in sample moisture content
- Soil and tissue data were natural log (ln) transformed
- Linear regression of ln transformed co-located Site soil-tissue paired data was completed
  - Analysis was conducted to identify if the degree of PFAS uptake was dependent on exposure level
- Then…

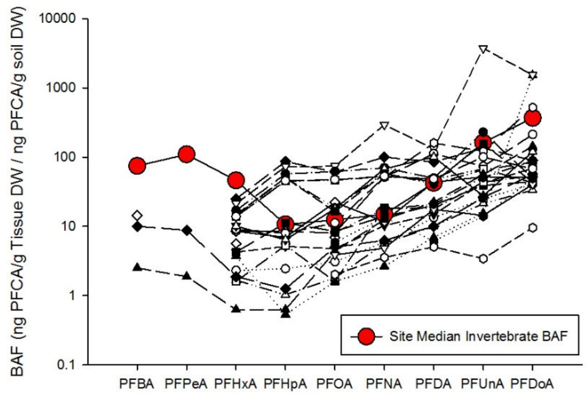
# PFAS Uptake Factor Identification

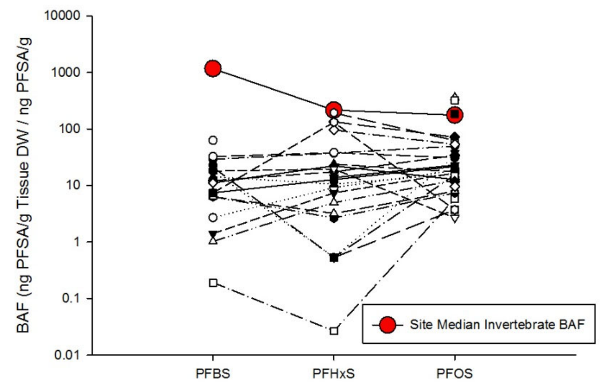
- A normality test of the ln transformed data was then conducted
  - This step was completed to ensure that the transformed data met assumptions regarding normality before simple regression modeling was performed

- The significance of the regression line was evaluated based on the following criteria[23]:
  - *The slope differed significantly [$p \leq 0.05$] from 0; and*
  - *The coefficient of determination ($R^2$) is greater than or equal to 0.2*

This presentation compares simple Site BCFs/BAF to literature values and identifies the importance for considering derivation of regression based uptake relationships

# Invertebrate Tissue BAF Literature Comparison



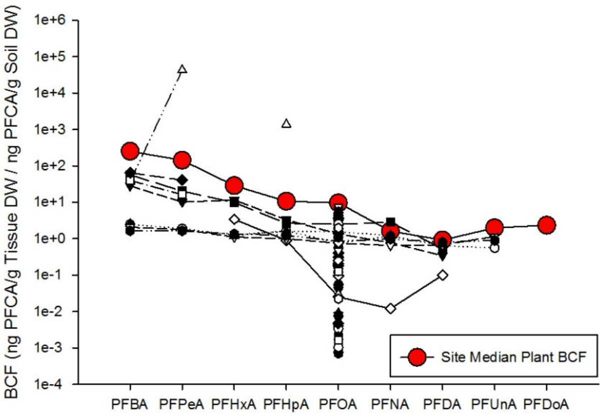

## PFCA

- Literature BAFs for individual PFCA are highly variable (approximately 2 orders of magnitude)
  - Site PFCA uptake exhibits a distinct relationship to carbon chain length
    - The Site uptake relationship is similar to that observed in other studies

## PFSA

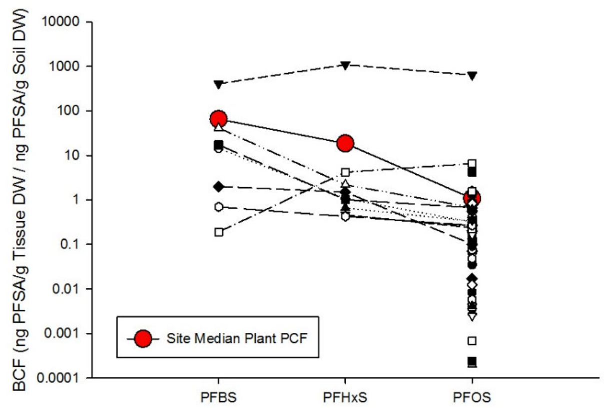
- Literature BAFs for individual PFSA are highly variable (up to approximately 4 orders of magnitude)
- PFSA uptake exceeds that of PFCA for compounds with equivalent carbon chain length
  - Site average PFSA uptake is high relative to literature values

# Plant Tissue BCF Literature Comparison




## PFCA

- Literature BCFs for individual PFCA vary significantly (in excess of 3 orders of magnitude for specific PFCA)
  - Site PFCA uptake exhibits a distinct relationship to carbon chain length
    - The Site uptake relationship is similar to that observed in other studies
    - Site PFCA uptake is high relative to literature based observations




## PFSA

- Literature BCFs for individual PFSA are highly variable (in excess of 3 orders of magnitude for specific PFSA)
- Site PFSA uptake magnitude decreases with increasing carbon chain length
  - Site average PFSA uptake is high relative to literature values

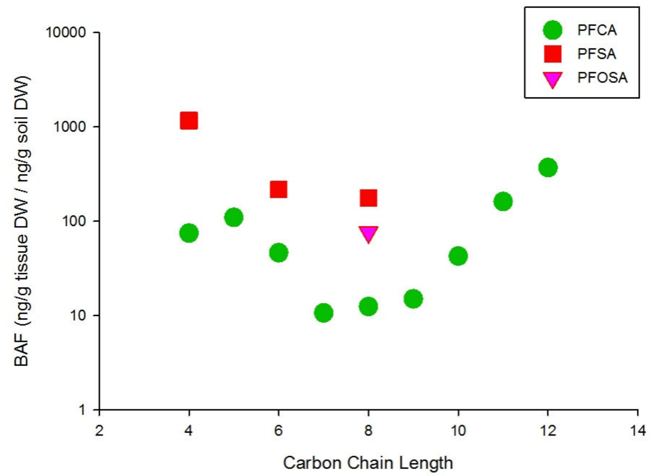
# Why are the Uptake Factors High?

- Many of the literature studies involved sludge amended soil.  The Site soil is aged and relatively sandy
  - Possibly greater sorption of PFAS in sludge amended soil resulting in lower bioavailability relative to Site soil
  - Possible differences in exchange capacity between Site and literature studies

- Many of the literature examples involved laboratory studies as opposed to field studies
  - Possibly equilibrium not fully achieved in certain laboratory studies

The Site study design did not allow for conclusive determination of the reason why the uptake factors were generally high, although the results identify that a “one size fits all” application of literature uptake factors in ecological risk analysis is not a preferable solution

# Invertebrate PFAS Uptake Controls




- PFAS uptake occurs through ingestion and dermal contact transfer from soil and soil pore-water
  - The initial PFCA BAF decrease followed by an increase at approximately $C_7$ has been attributed to different soil sorption mechanisms dependent upon PFCA chain length, resulting in differences in bioavailability[5]
  - An inverse BAF vs. PFSA carbon chain length relationship is present and has been observed in other studies[5, 10]. This relationship may result from the higher soil sorption affinity for longer chain PFSA relative shorter chain PFSA which decrease bioavailability[10]

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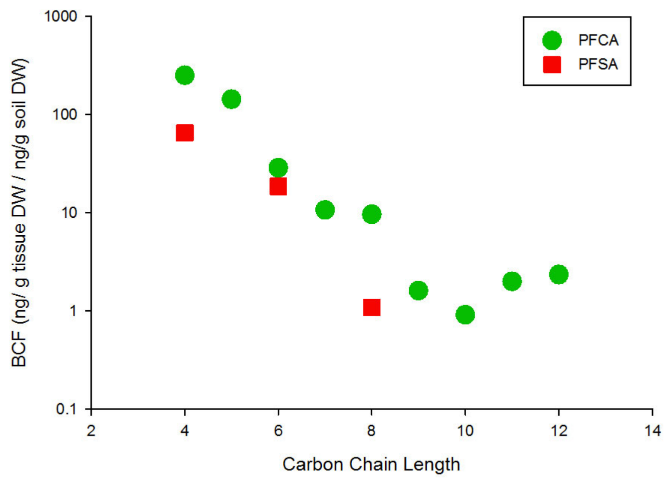
# Plant PFAS Uptake Controls




## Plants

- For uptake and translocation to occur, PFAS in soil pore-water must transfer through a series of root barriers and enter the xylem
  - Water mediated process and the degree of translocation is anticipated to be controlled by chemical hydrophobicity due to the nature of lipid root membranes
- PFAS are water soluble and hydrophobicity increases with carbon chain length
  - Soil (organic carbon) and root surface sorption affinity increases with carbon chain length
- PFAS are essentially non-volatile, therefore accumulate in plant tissue rather than being transpired

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# Site Specific Target Level Considerations

## Literature PFAS Uptake and Translocation Potential[22]

$$Root > Straw > Seeds \geq SeedHusks$$

- Plant PFAS uptake magnitude is vegetative compartment specific
  - CCME[17] adjusted plant BCFs with a harvest index to identify a geometric mean weighted BCF for PFOS of 0.35. This is more than 3 orders of magnitude lower than the highest value presented earlier (fern leaf) and approximately 1 order of magnitude lower than the Site average PFOS BCF (whole plant-aboveground)
  - PFAS may preferentially partition to leaf portions of an above-grade plant tissue[5, 20] as opposed to storage compartments in some cases
  - Protein content differences between plant species may influence PFAS BCFs

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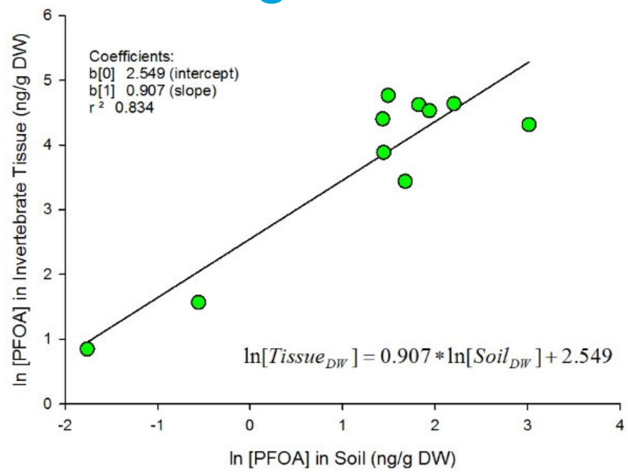
# Site Specific Target Level Considerations




- The magnitude of PFAS uptake may be soil concentration dependent
  - An inverse PFCA soil concentration *vs.* invertebrate BAF has been observed[8] and a positive PFOS, PFOA *vs.* exposure concentration correlation has been observed for various plants[20, 22] in the literature.
- Consider identifying if a soil concentration dependent tissue PFAS concentration relationship is present at your investigation area(e.g. 21)
  - Site invertebrate tissue PFAS concentrations *vs.* soil concentrations are positively correlated
  - Site plant tissue PFAS concentrations *vs.* soil concentrations are mixed positively or negatively correlated, although $r^2$ indicates generally a poor fit

# Site Specific Target Level Considerations

$$SSTL_{soil} = EPC_{soil} \bullet \frac{THQ}{HQ} = C_{soil} \bullet \left( \frac{THQ}{\left[ \left( \frac{A}{HR} \right) \bullet \left( \frac{IR_{plant} \bullet C_{soil} \bullet BCF_{soil-plant}}{BW} \right) \right] / TRV} \right)$$

| BCF (soil to plant) | $SSTL_{soil}$ |
|---|---|
| 643 (DW) – maximum literature value | 1.7 ng/g |
| 1.1 (DW) – Site median | 992 ng/g |
| 1.00 (DW) – Site BCF at 100 ng/g PFOS in soil. Based on correlation | 1090 ng/g |
| 0.35 (DW) – CCME, 2017[17] | 3117 ng/g |

- Significant variability in literature uptake factors = potential significant variability in derived SSTLs
  - Site tissue sampling with co-located soil analysis should be considered for a detailed quantitative risk analysis.
  - Comparison of Site soil PFAS exposure levels, soil properties (i.e. organic carbon content) and Site plant species present to literature data should be considered if selecting uptake factors for use in a preliminary quantitative/screening level risk analysis.

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SSTL equation assumes herbivore exposure without soil ingestion, for illustrative purposes. SSTLs calculated assuming the Meadow vole represents the feeding guild measurement receptor

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