

# The Role of Precursor Transformation on PFAS Fate and Transport in the Saturated Zone



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Emily Stockwell, PE

# Acknowledgements

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Dr. Dave Adamson, GSI

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Poonam Kulkarni, GSI

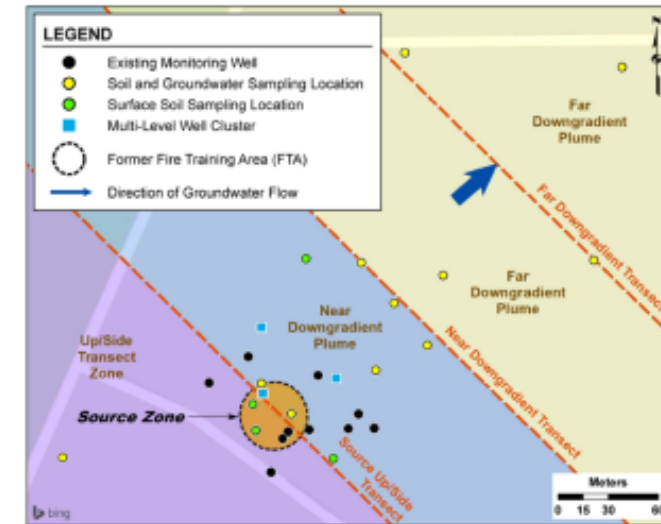
Dr. Shahla Farhat, GSI



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# Objectives

- › Combine high-resolution field characterization data with semi-analytical modeling
- › Determine relative transformation rates of different PFAS classes
- › Document key fate and transport parameters at an AFFF release site
- › Establish how precursor transformation influences PFAS plume development

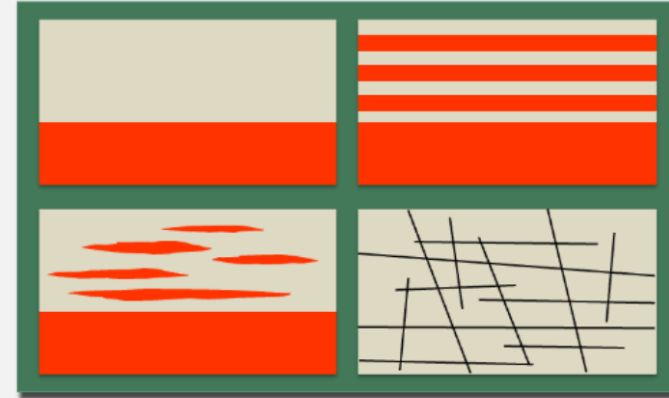


# REMChlor-MD Overview

- › Semi-analytical model
- › Free, available via ESTCP website
- › Easy to use for non-modelers
- › Simulates:
  - › Matrix diffusion
  - › Retardation
  - › Molecular diffusion
  - › Plume degradation
  - › Dispersion
  - › Source zone remediation

## REMChlor-MD

Evaluating Matrix Diffusion for Chlorinated Solvents  
Version 1.0



**REMChlor-MD Data Input Screen** Version 1.0 Beta

Site Location and ID:

1. **STARTING INFORMATION** ☒ SI Units ☐ English Units ☐ Unconsolidated ☐ Fractured Rock/Media

2. **MODEL CONFIGURATION**

Cell Size: X-Direction (in direction of groundwater flow)  (m) Y-Direction (transverse to groundwater flow)  (m) Z-Direction (vertical) (all layers have same hydrogeology)  (m)

Model Size: X-Value  (m) Y-Value  (m) Bottom of Screen  (m) Starting Year of Simulation (year the source started)  (YYYY year) Ending Year of Simulation  (YYYY year)

3. **MEDIA CHARACTERISTICS** (uniform for all cells)

Soil Type:  Hydr. Cond. (cm/sec)  Porosity (-)  Tortuosity (-)  Low Permeability Zone (Low-k)    Default Tortuosity

T-Zone Hydraulic Gradient  (-) T-Zone Groundwater Darcy Velocity  (m/yr)

4. **MATRIX DIFFUSION**

Calculate Heterogeneity

Average Darcy Velocity (including low-k units)  (m/yr) Transmissive Zone Volume Fraction  (%) Average Diffusion Length  (m) Surface Area of Low-k Interfaces  (m<sup>2</sup>)

5. **CONTAMINANTS AND SOURCE TERM**

Constituent (use dropdown menu)  Parent  Deg. Prod. 1  Deg. Prod. 2  Deg. Prod. 3  Initial Source Concentration  Retardation Factor in T-Zone  (m) Retardation Factor in Low-k  (m) Source Width (REMChlor-MD will round to nearest whole cell)  (m) Z-Value for Top of Source (model bottom is at 340)  (m) Z-Value for Bottom of Source  (m) General Molecular Diffusion Coefficient for all Constituents  (m<sup>2</sup>/day)

6. **PLUME DEGRADATION** (Both T-Zone and Low-k Zone)

Model ends here → Time Period 2 (T2) → Time Period 1 (T1) → Model starts here →

7. **PLUME TRANSPORT**

Dispersivity (m)  Longitudinal  Transverse  Vertical

8. **SOURCE ZONE REMEDIATION**

Percent Source Mass Removed by Remediation  (%) Remediation Started in Year  (YYYY) Remediation Ended in Year  (YYYY) Mass-Flux/Remaining-Mass Term (Gamma, Γ)  (-) Natural Source Decay Rate  (1/yr)

9. **MODELING PARAMETERS**

Time-step Size  (yr) Maximum Number of Iterations  (-) Convergence Tolerance  (μg/L) See Results Every  (yr)

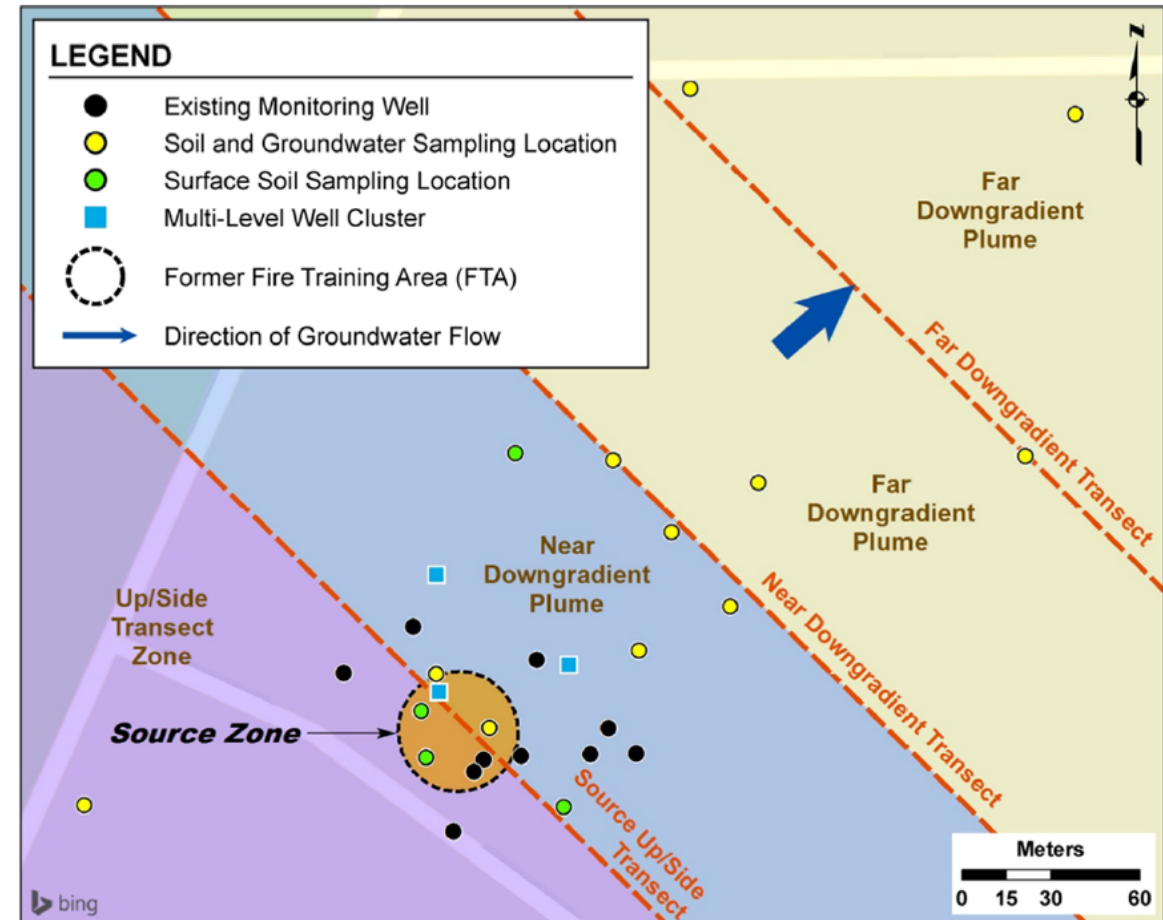
Next Step:

# Field Site Overview

- › High-resolution sampling at 11 locations
  - › Groundwater at ~5 depths
  - › Soil at ~ 10 depths
- › Analysis for 79 PFAS in Groundwater (Dr. Field, Oregon State University)
  - › 57 Precursors
  - › 22 PFAAs
- › Analysis for 136 PFAS in Soil (Dr. Higgins, Colorado School of Mines)
  - › 115 Precursors
  - › 21 PFAAs

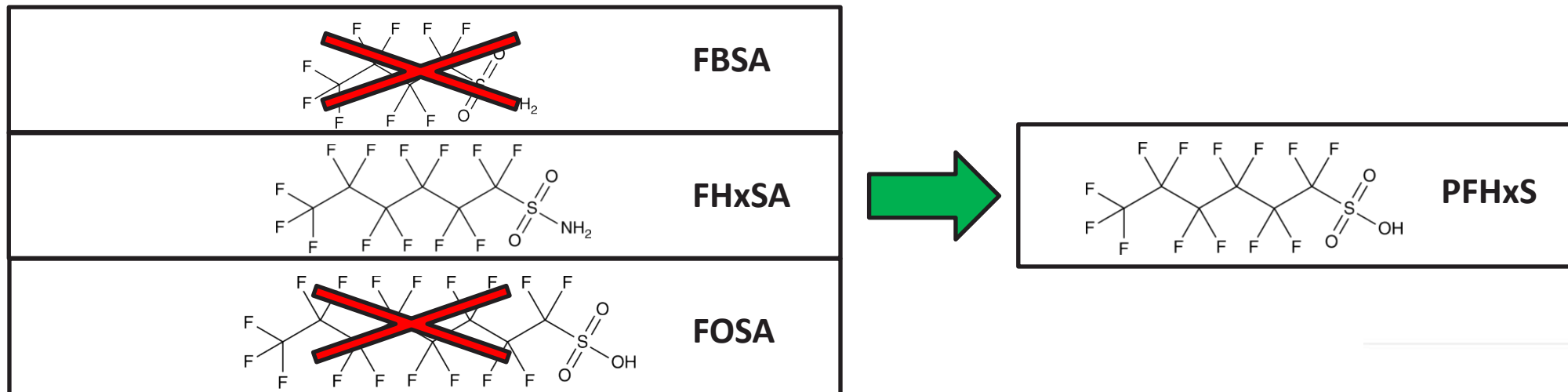
## Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas

David T. Adamson,\* Anastasia Nickerson, Poonam R. Kulkarni, Christopher P. Higgins, Jovan Popovic, Jennifer Field, Alix Rodowa, Charles Newell, Phil DeBlanc, and John J. Kornuc



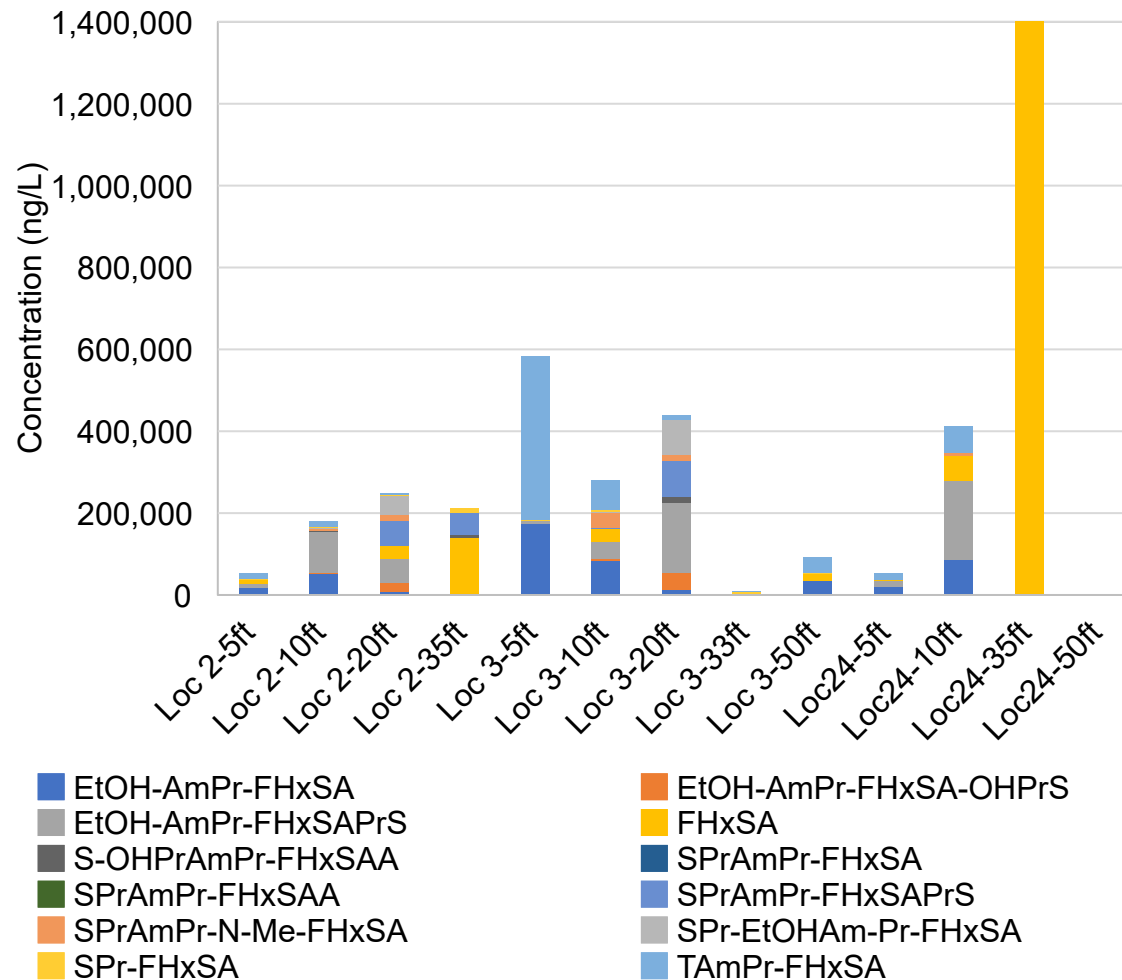
# Key Assumptions For Incorporating Precursor Transformation into REMChlor-MD

- › The PFAS identified in the data set represent all PFAS at the site
  - › In groundwater, the 57 identified precursors represent all precursors
  - › In soil, the 115 identified precursors represent all precursors
- › “**PFOS-able precursors**” are PFSA precursors with 8 fully fluorinated carbons
- › “**PFOA-able precursors**” are PFCA precursors with 7 or 8 fully fluorinated carbons
- › “**PFHxS-able precursors**” are PFSA precursors with 6 fully fluorinated carbons
- › “**PFBS-able precursors**” are PFSA precursors with 4 fully fluorinated carbons

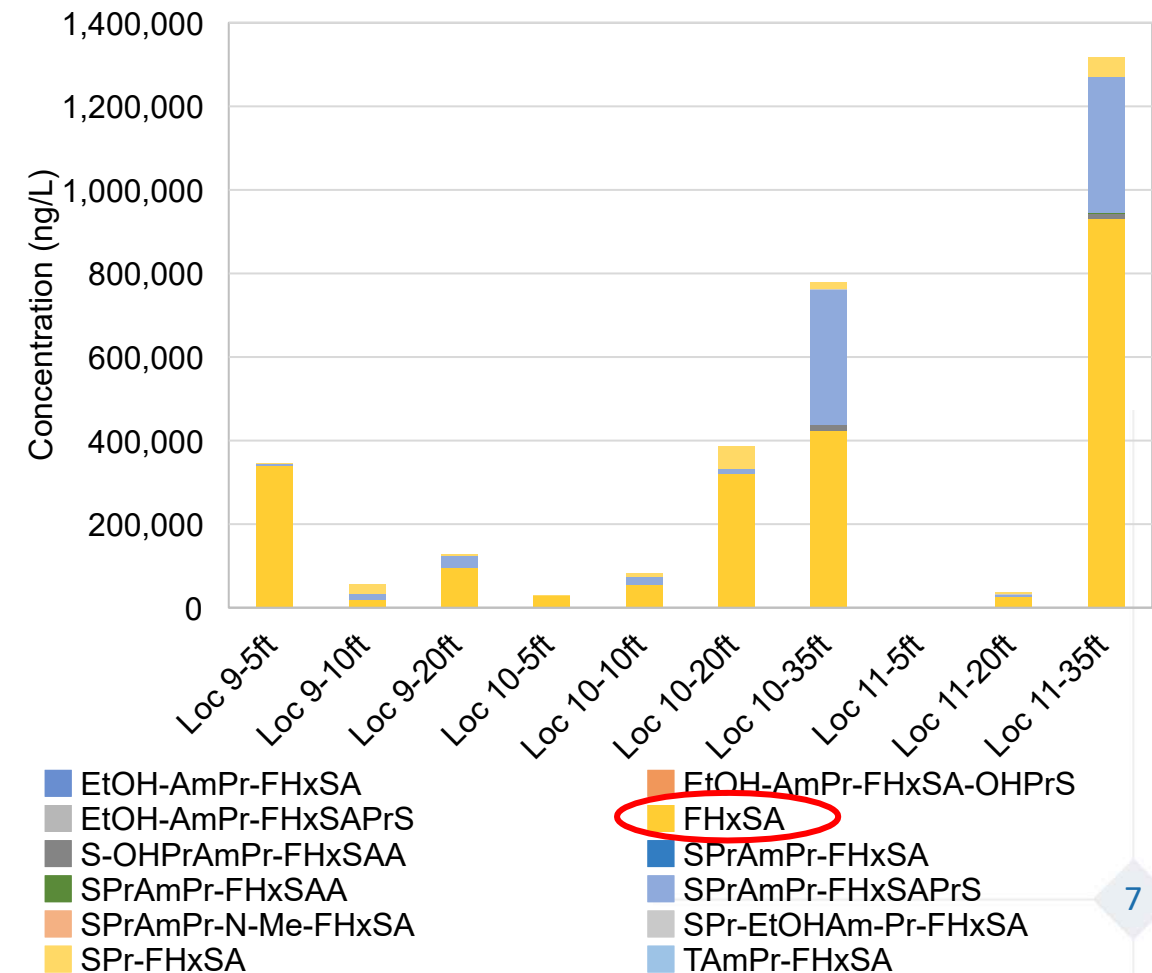


# Field Site PFHxS-able Precursors in Groundwater

## PFHxS-able Precursors in Source Area Groundwater

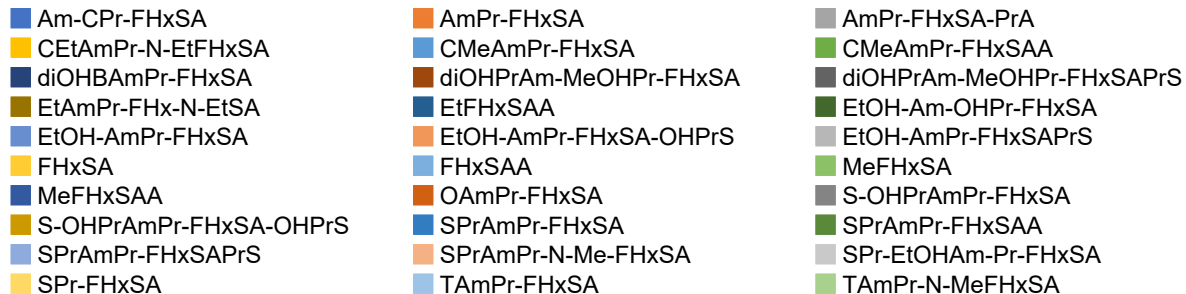
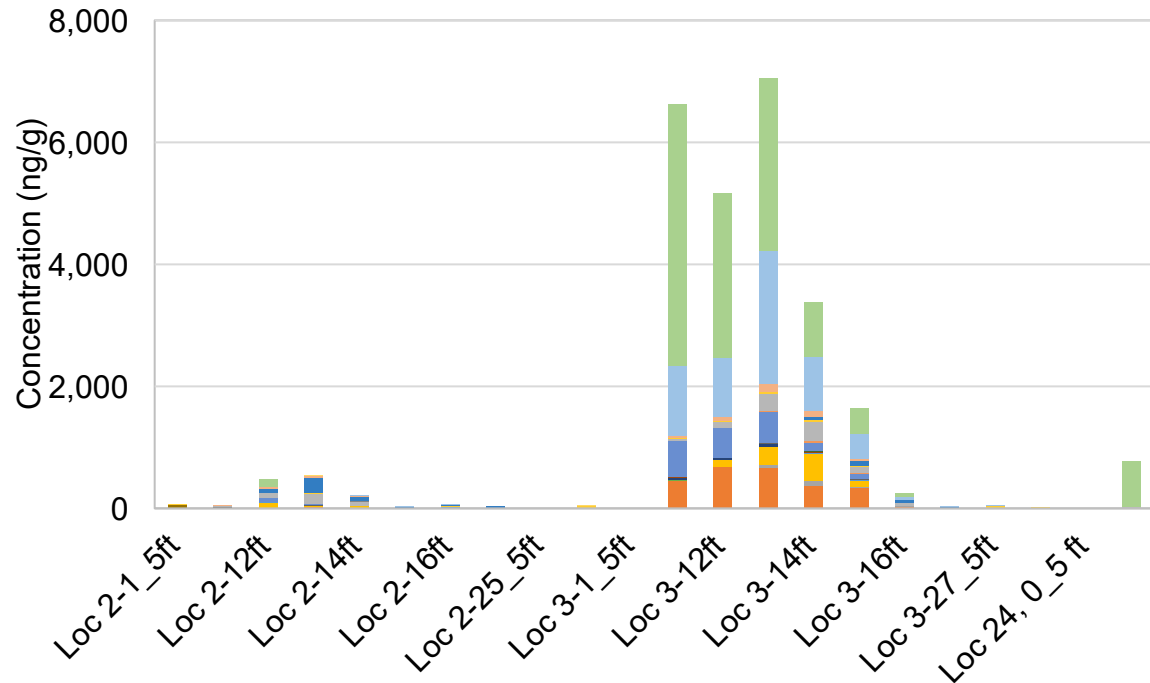


## PFHxS-able Precursors in Mid-Plume Groundwater

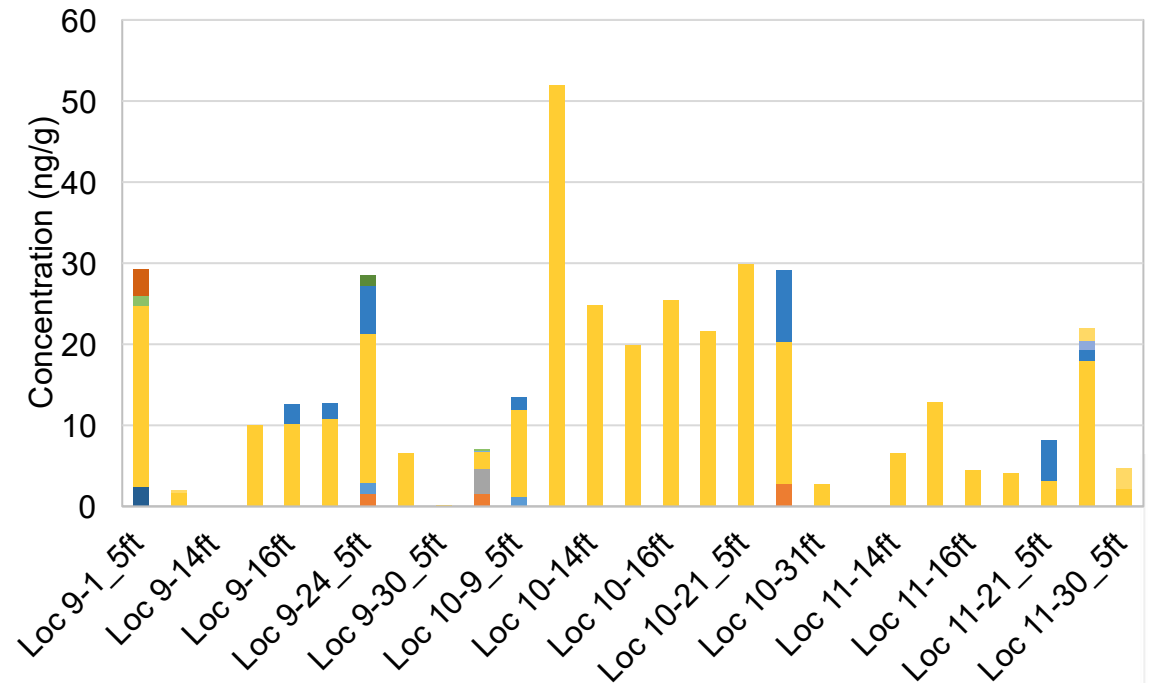


# Field Site PFHxS-able Precursors in Soil

## PFHxS-able Precursors in Source Area Soil

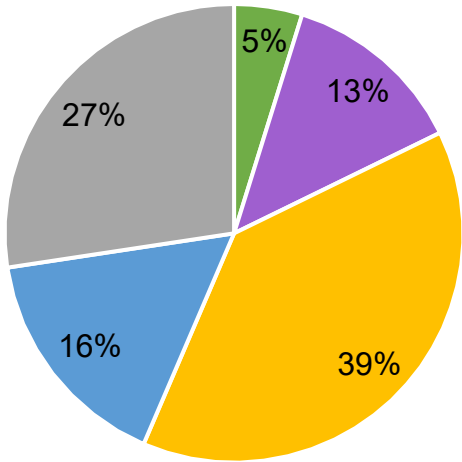


## PFHxS-able Precursors in Mid-Plume Soil



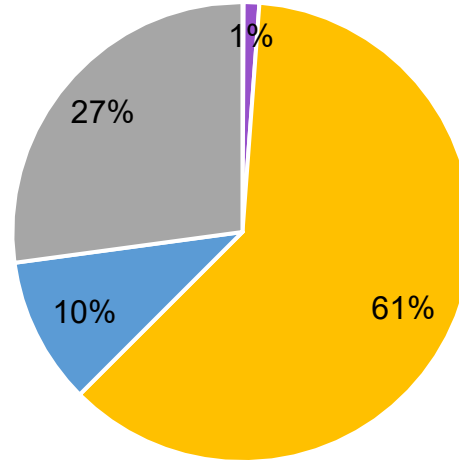
# Field Site Precursor Characterization

Source Area Groundwater

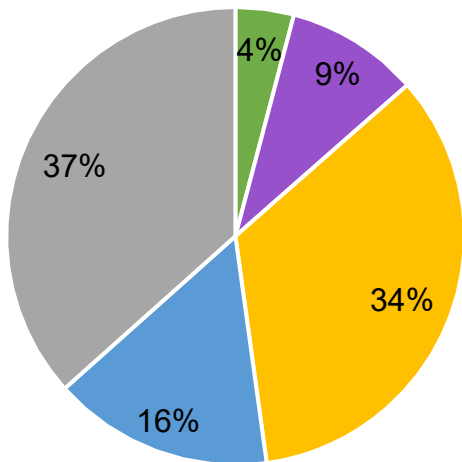


Groundwater Flow  
→

Mid-Plume Groundwater

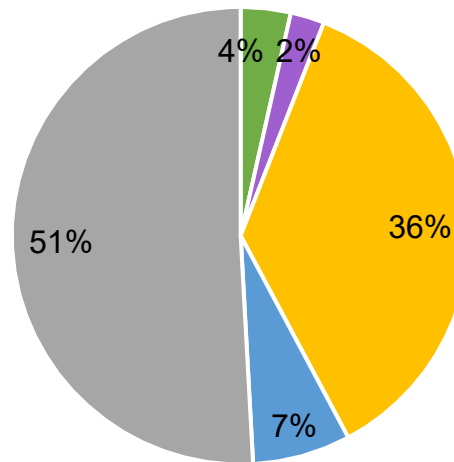


Source Area Soil



Groundwater Flow  
→

Mid-Plume Soil



Precursor mass by proportion:

- PFHxS-able
- PFBS-able
- PFOA-able
- PFOS-able

# Field Site Model Inputs

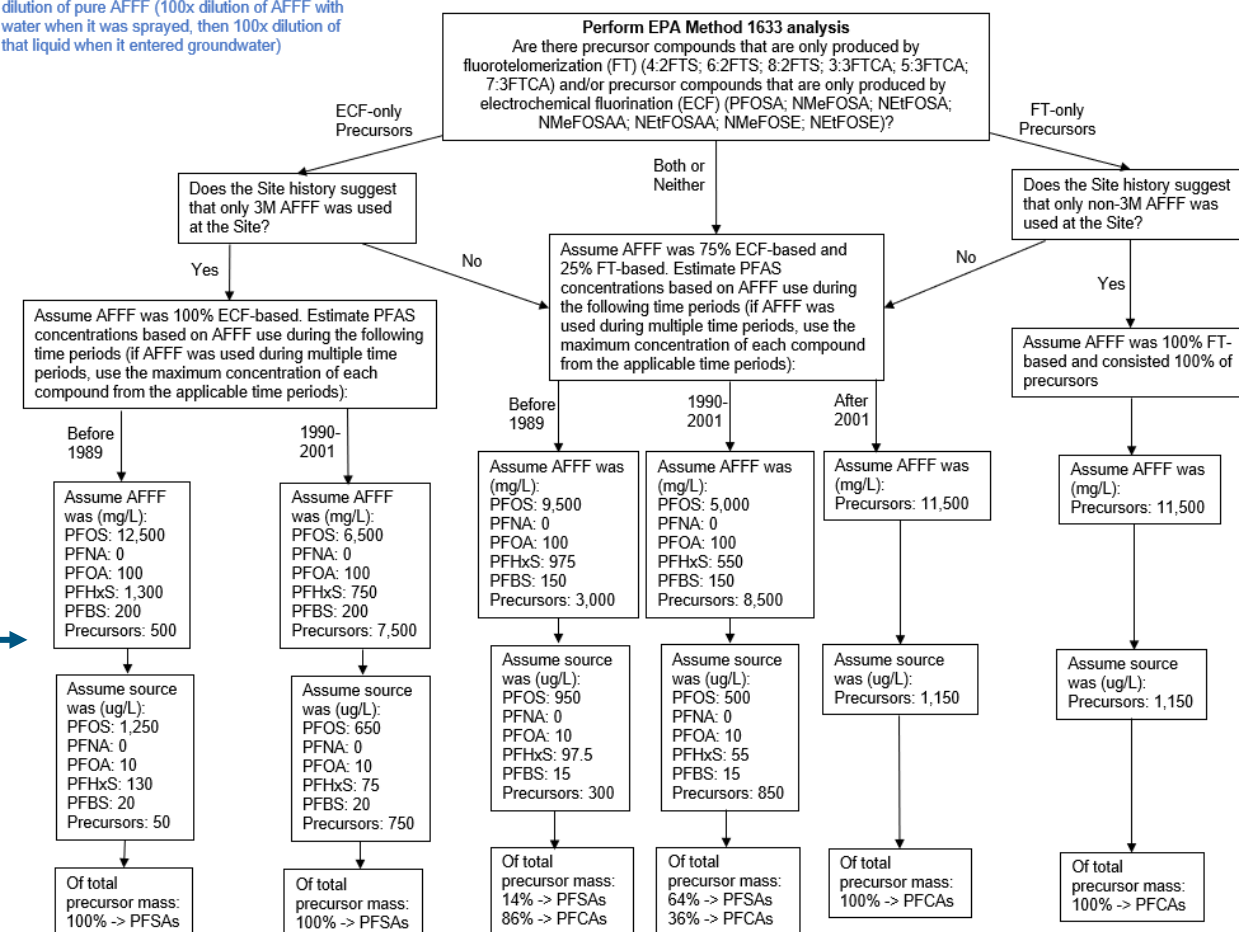
- › Soil and Groundwater Properties
- › Molecular Diffusion Coefficients
- › Precursor Yields
- › Source Mass at Time of Release
- › Retardation Factors\*
- › Precursor Transformation Rates\*
- › Initial Source Concentrations\*

\* Calibration parameter

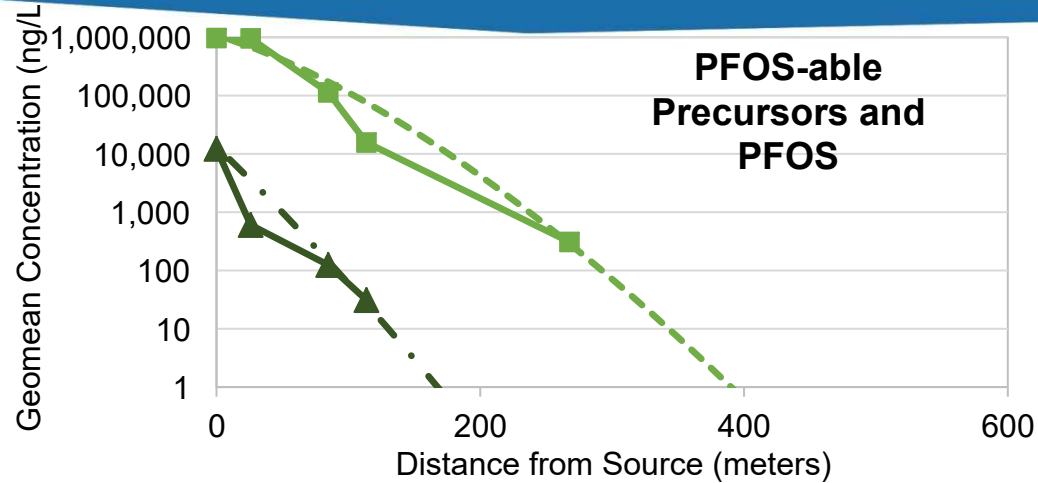
## Source Concentration Estimation Method

All source concentrations assume 10,000x dilution of pure AFFF (100x dilution of AFFF with water when it was sprayed, then 100x dilution of that liquid when it entered groundwater)

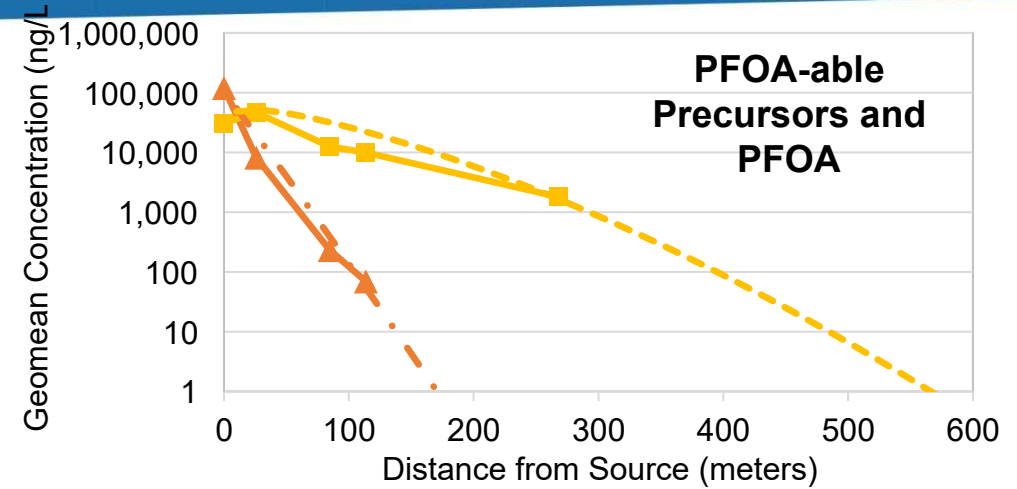
### AFFF Source Concentration Estimation Flow Chart



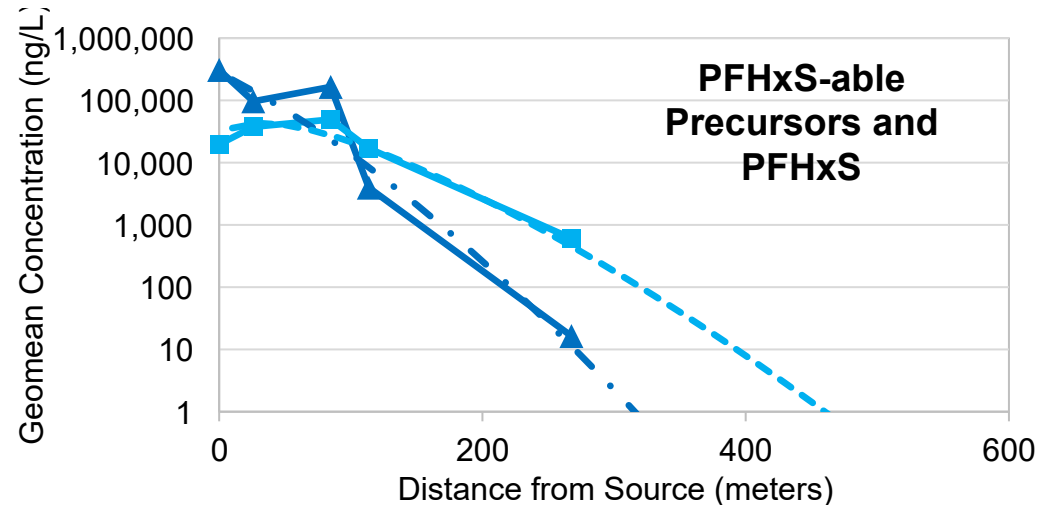
# Field Site Model Calibration



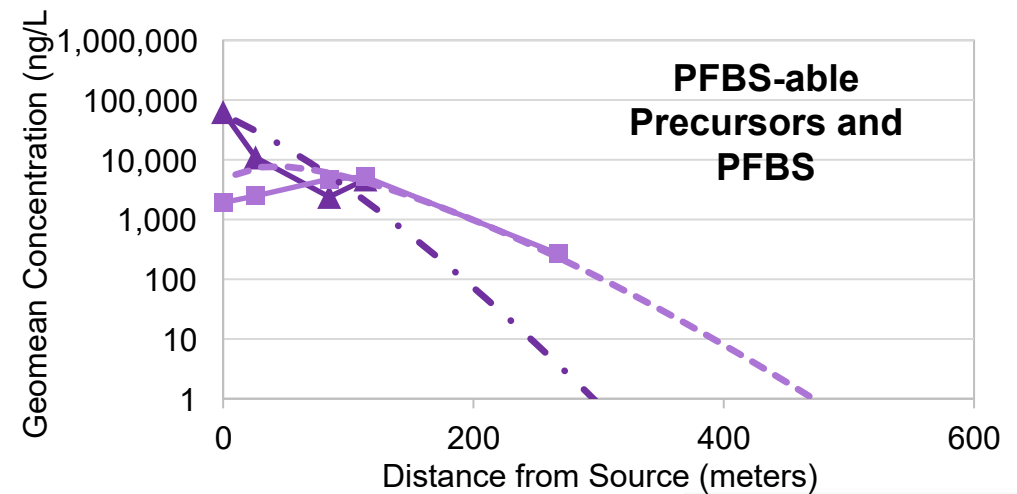
▲ PFOS-able Precursors      ■ PFOS  
- • - Modeled PFOS-able Precursors      - - - Modeled PFOS



▲ PFOA-able Precursors      ■ PFOA  
- • - Modeled PFOA-able Precursors      - - - Modeled PFOA

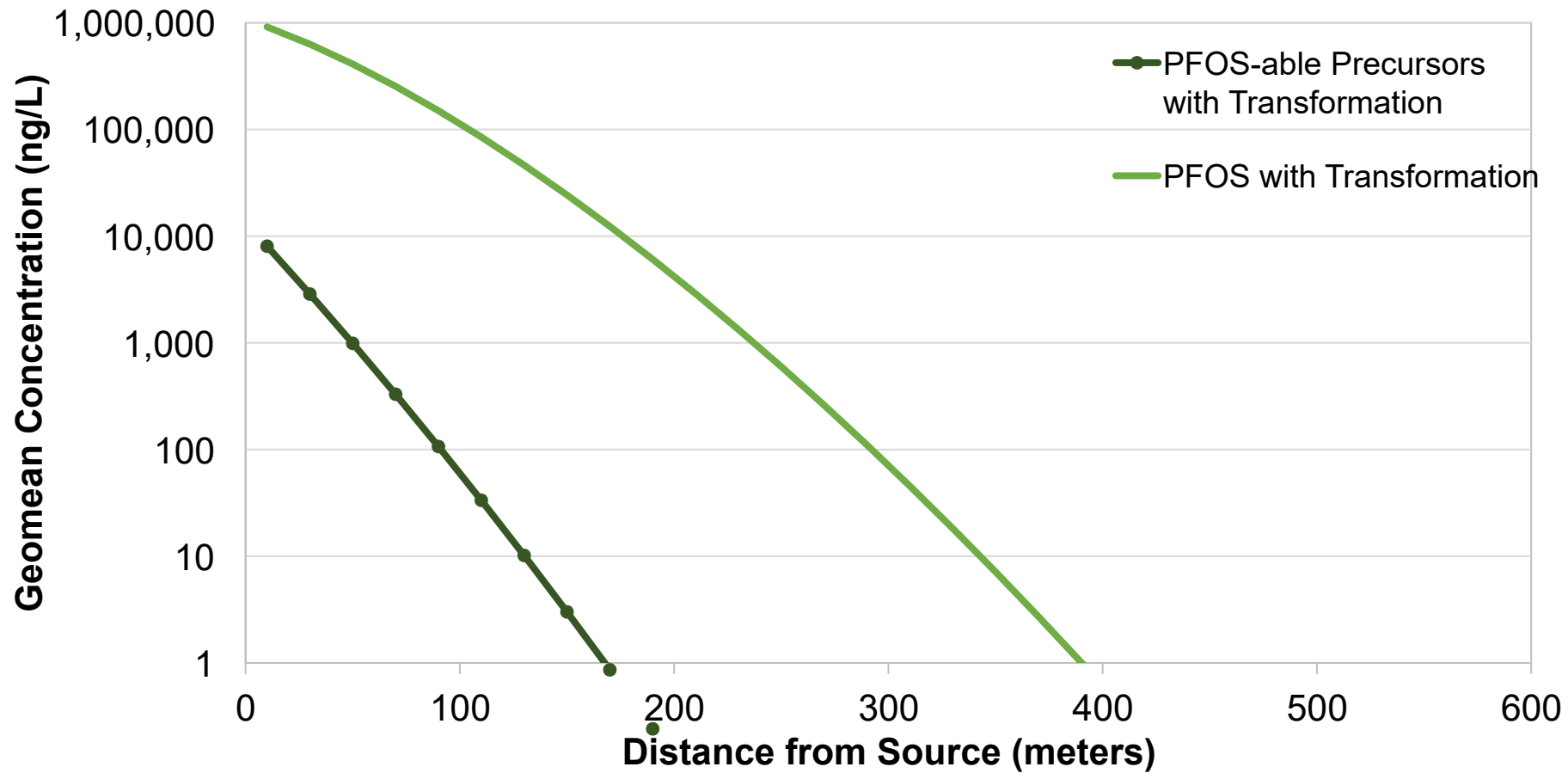


▲ PFHxS-able Precursors      ■ PFHxS  
- • - Modeled PFHxS-able Precursors      - - - Modeled PFHxS

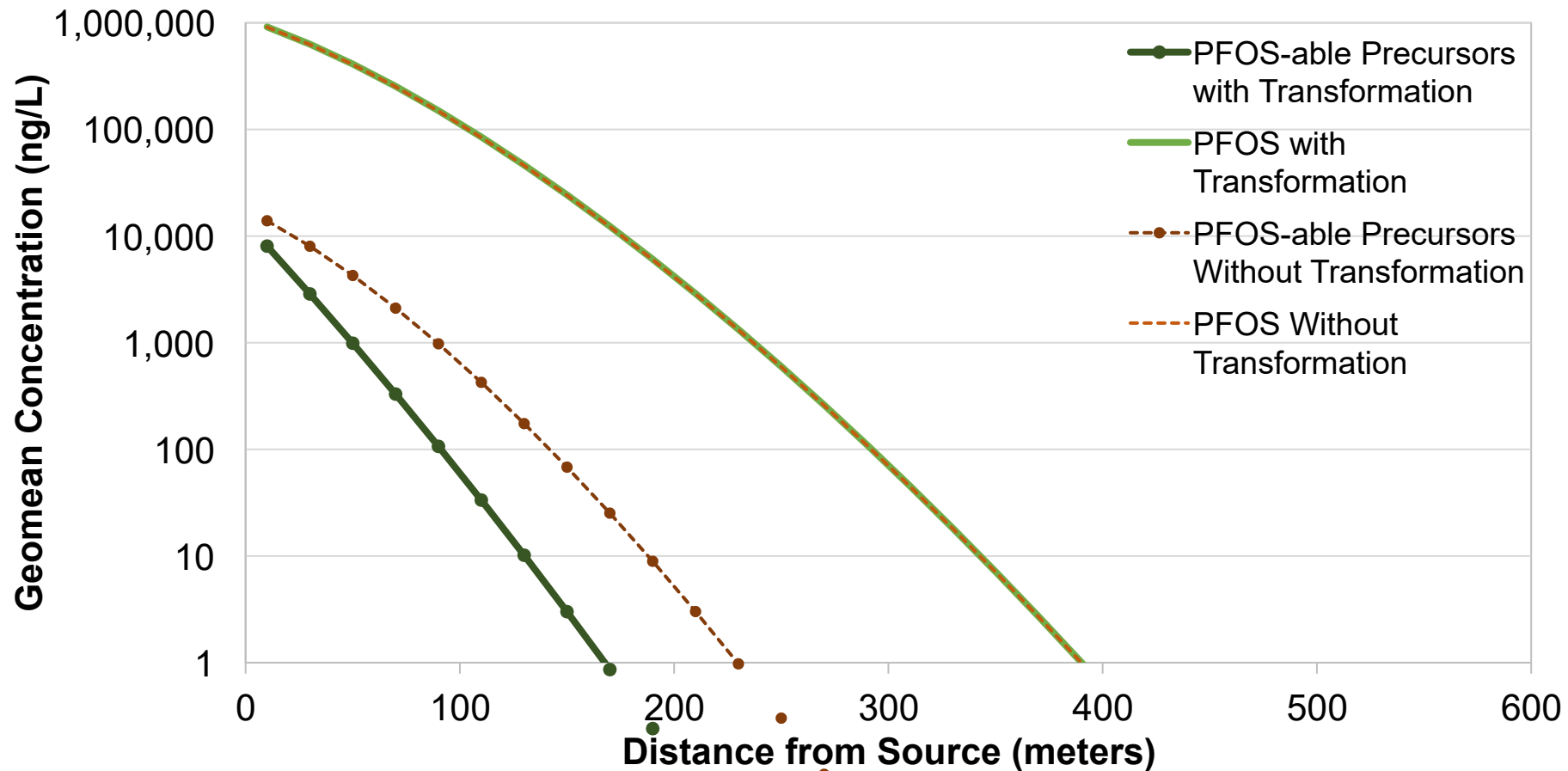


▲ PFBS-able Precursors      ■ PFBS  
- • - Modeled PFBS-able Precursors      - - - Modeled PFBS

# Field Site PFOS Model – Year 40

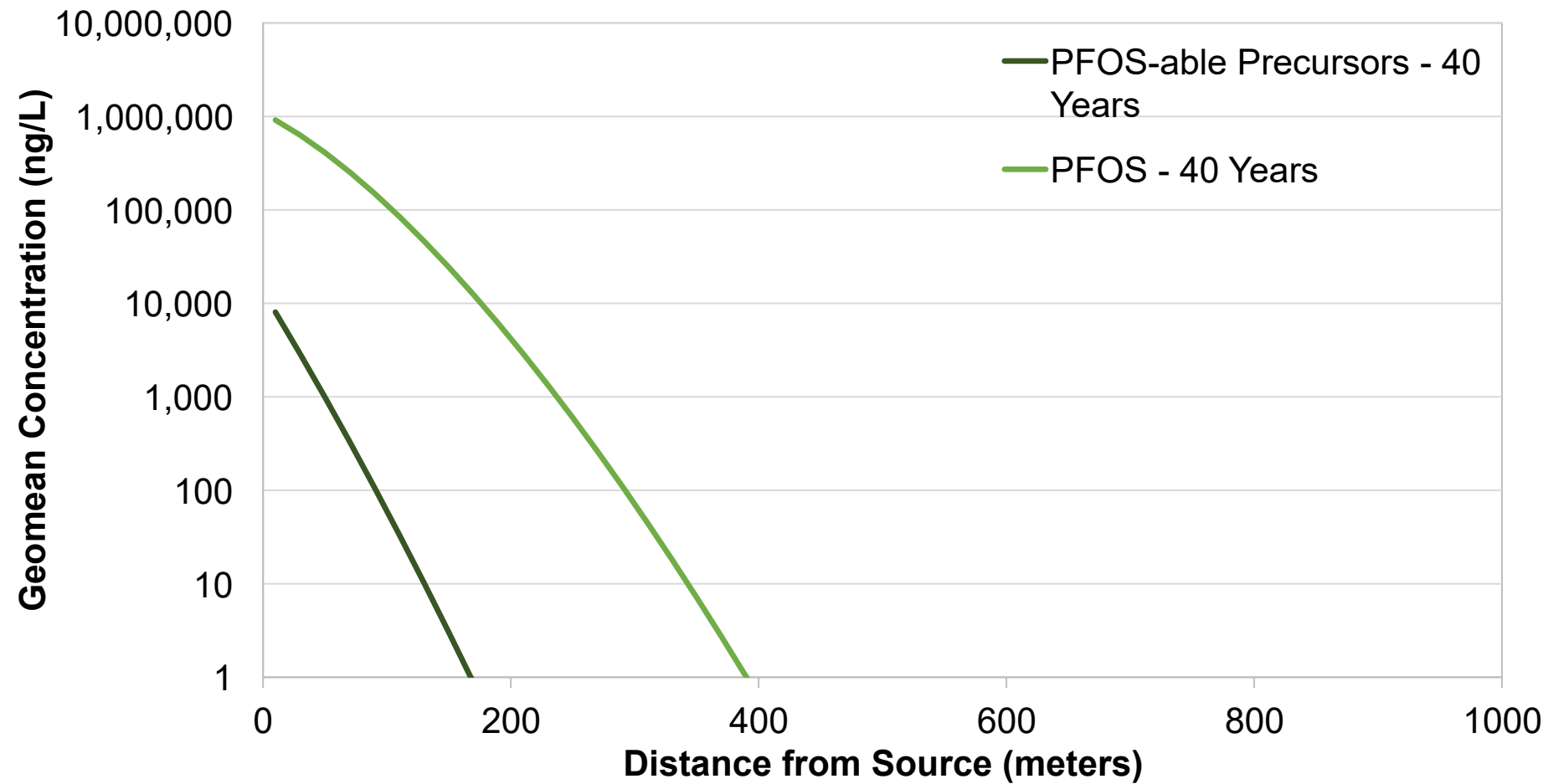


# Field Site PFOS Model – Year 40

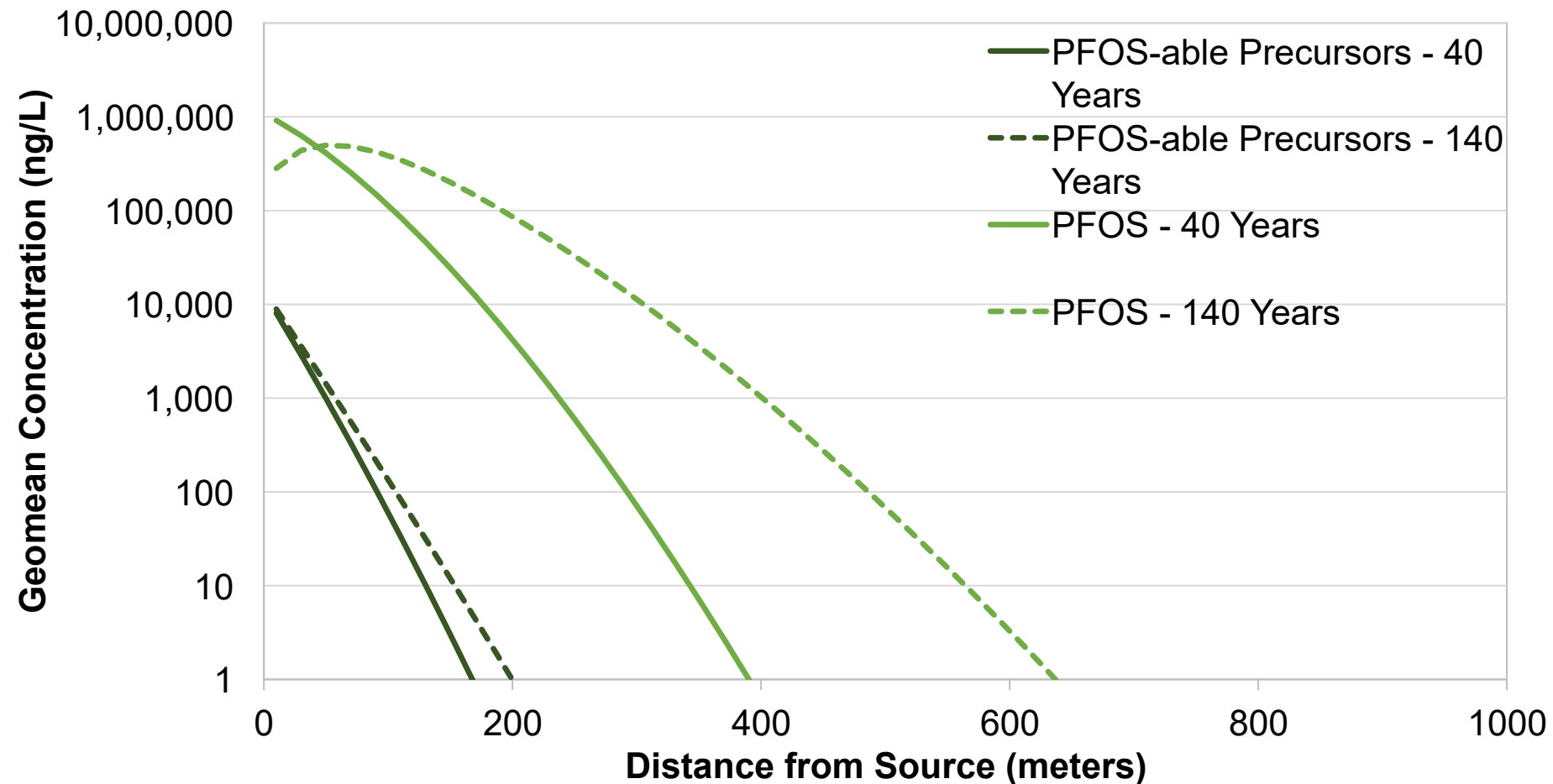


Even though PFOS-able precursor transformation occurs, the concentrations of PFOS are so much higher that precursor transformation has no impact on PFOS plume length or concentration

# Field Site PFOS Model – Year 40

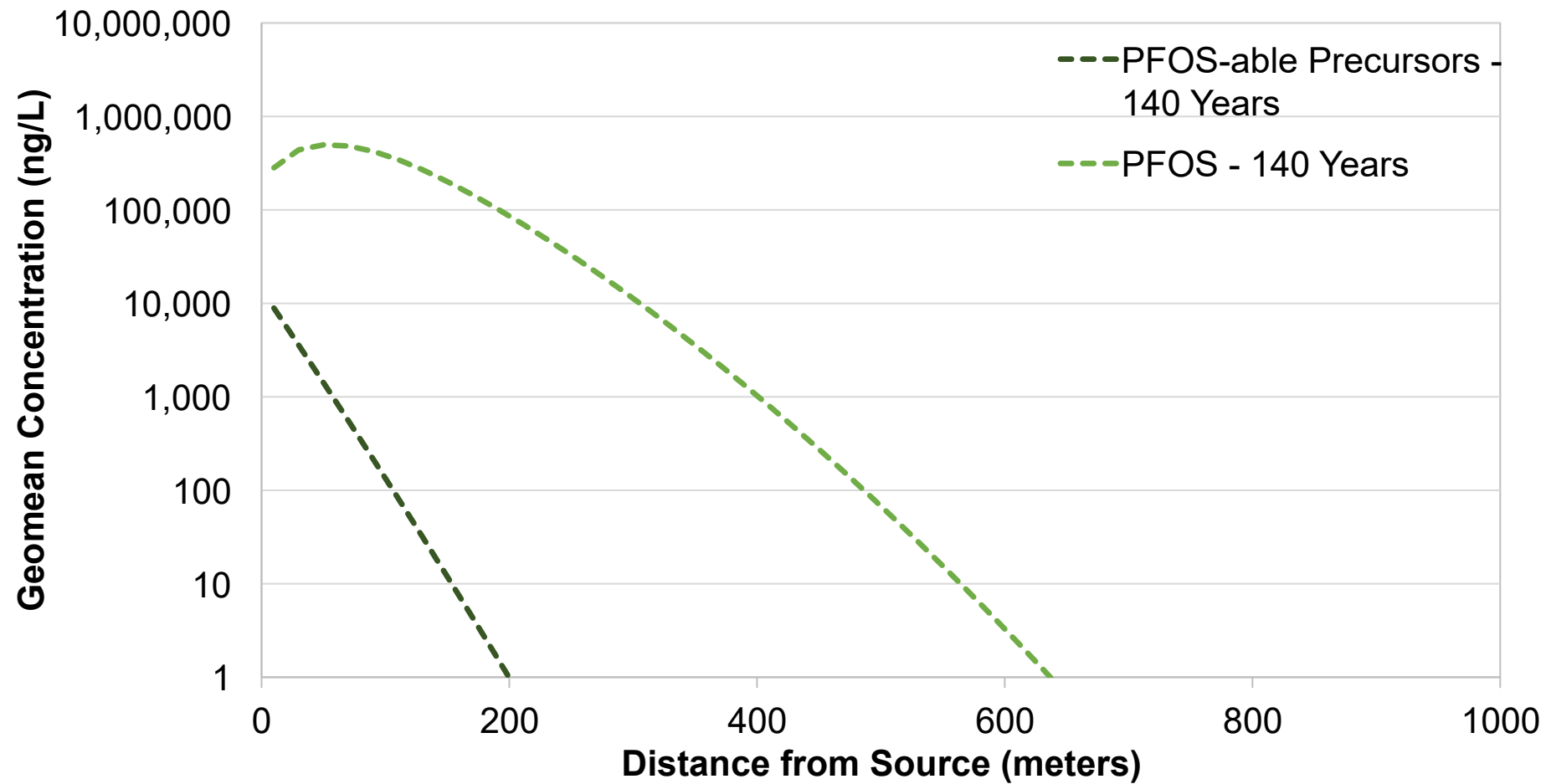


# Field Site PFOS Model – Year 140

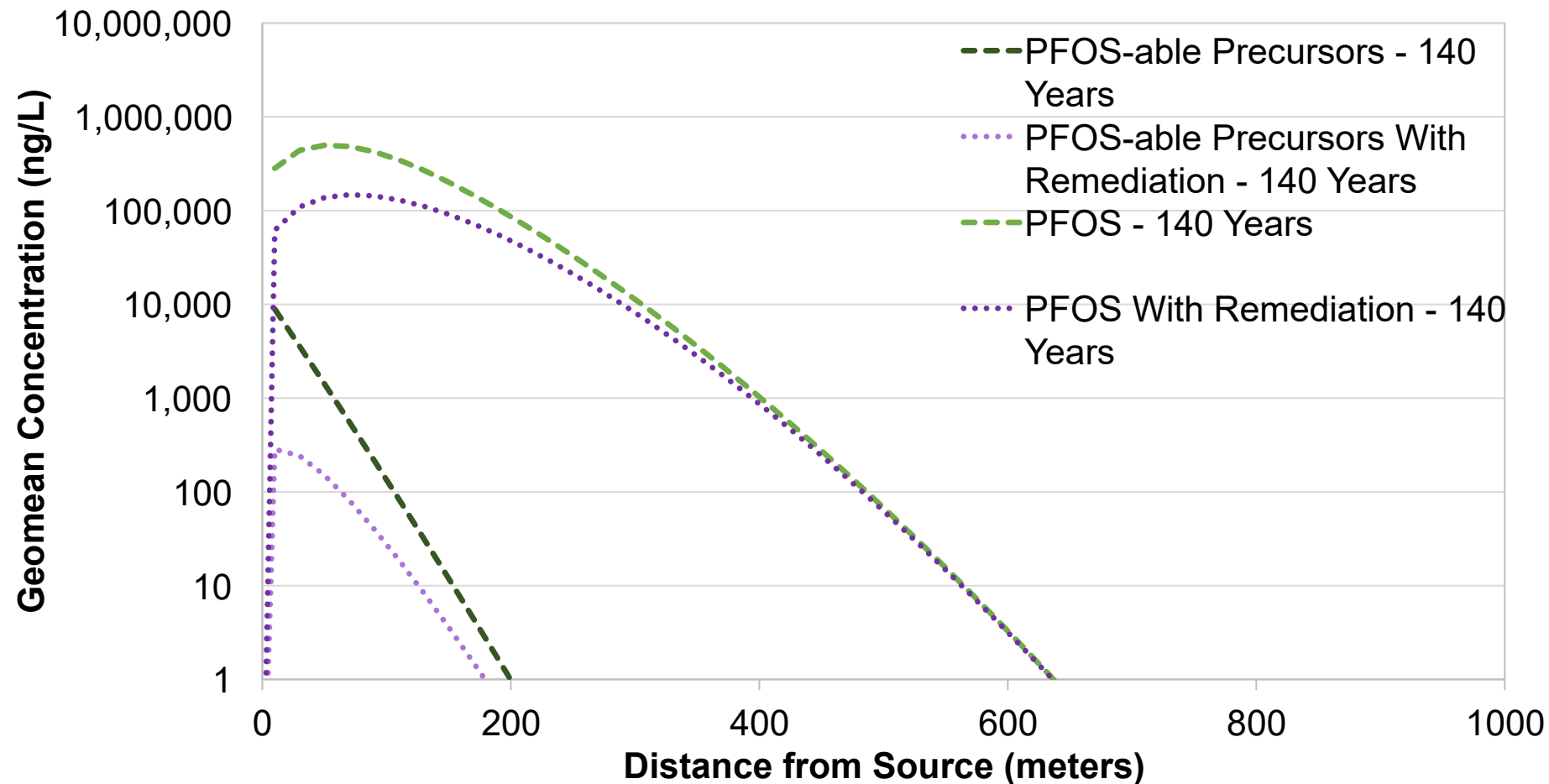


**PFOS-able precursor and PFOS plumes are still expanding due to continued release from source zone and migration of downgradient plume**

# Field Site PFOS Model – Year 140

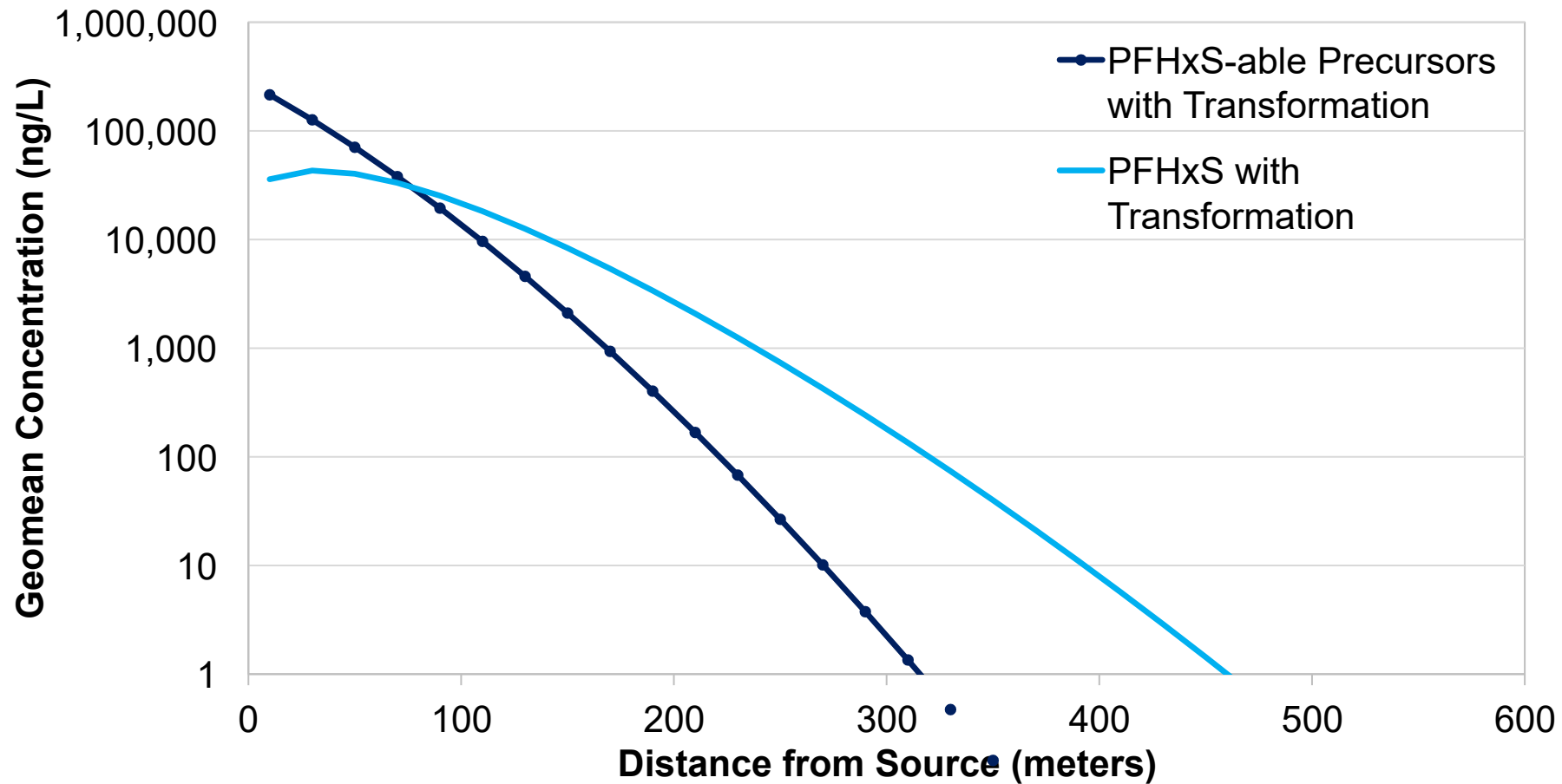


# Field Site PFOS Model – Year 140, With Source Remediation at Year 40

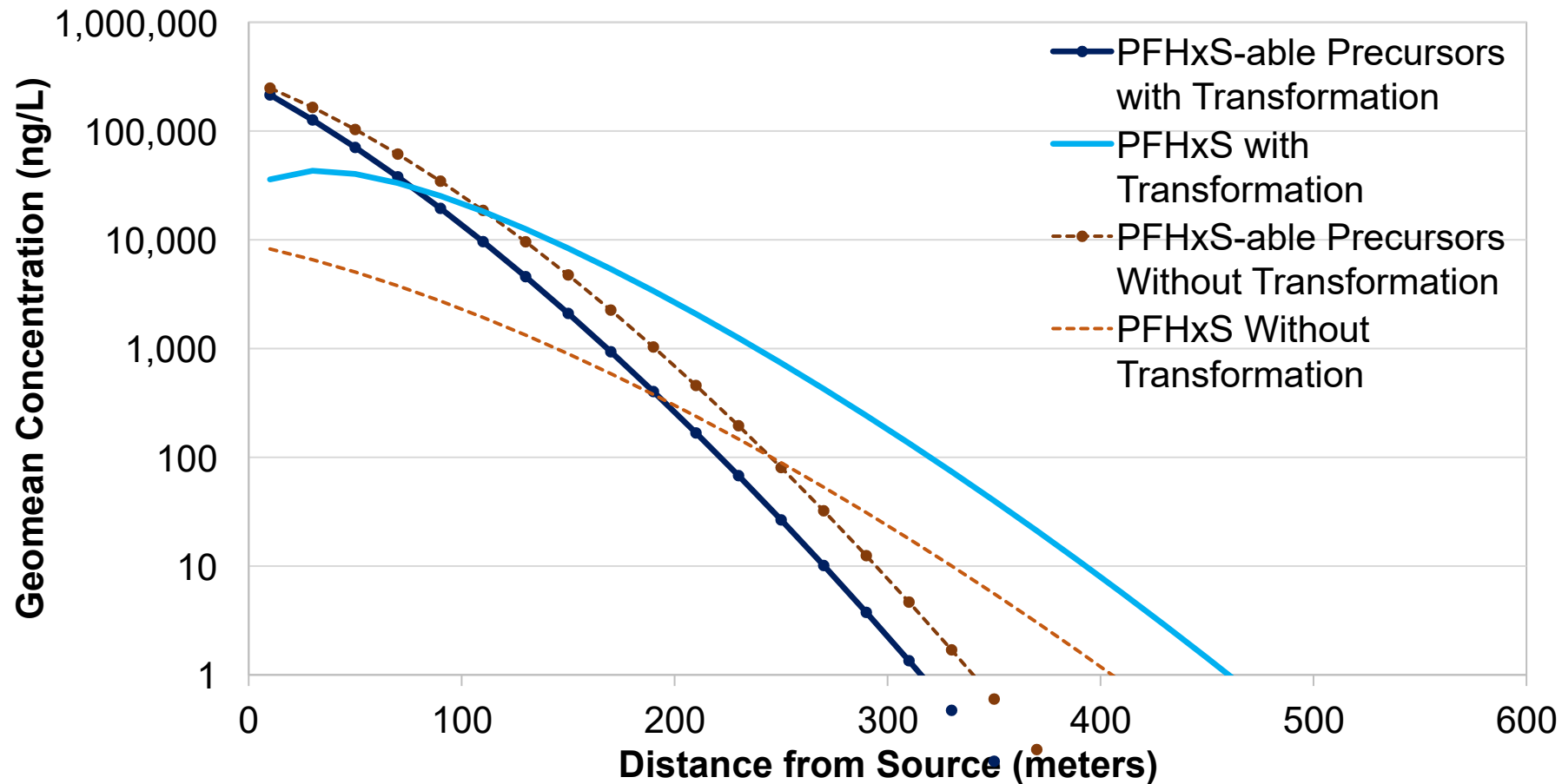


**Source concentrations decrease, but plumes persist and continue to expand downgradient due to continued migration of downgradient plume**

# Field Site PFHxS Model – Year 40

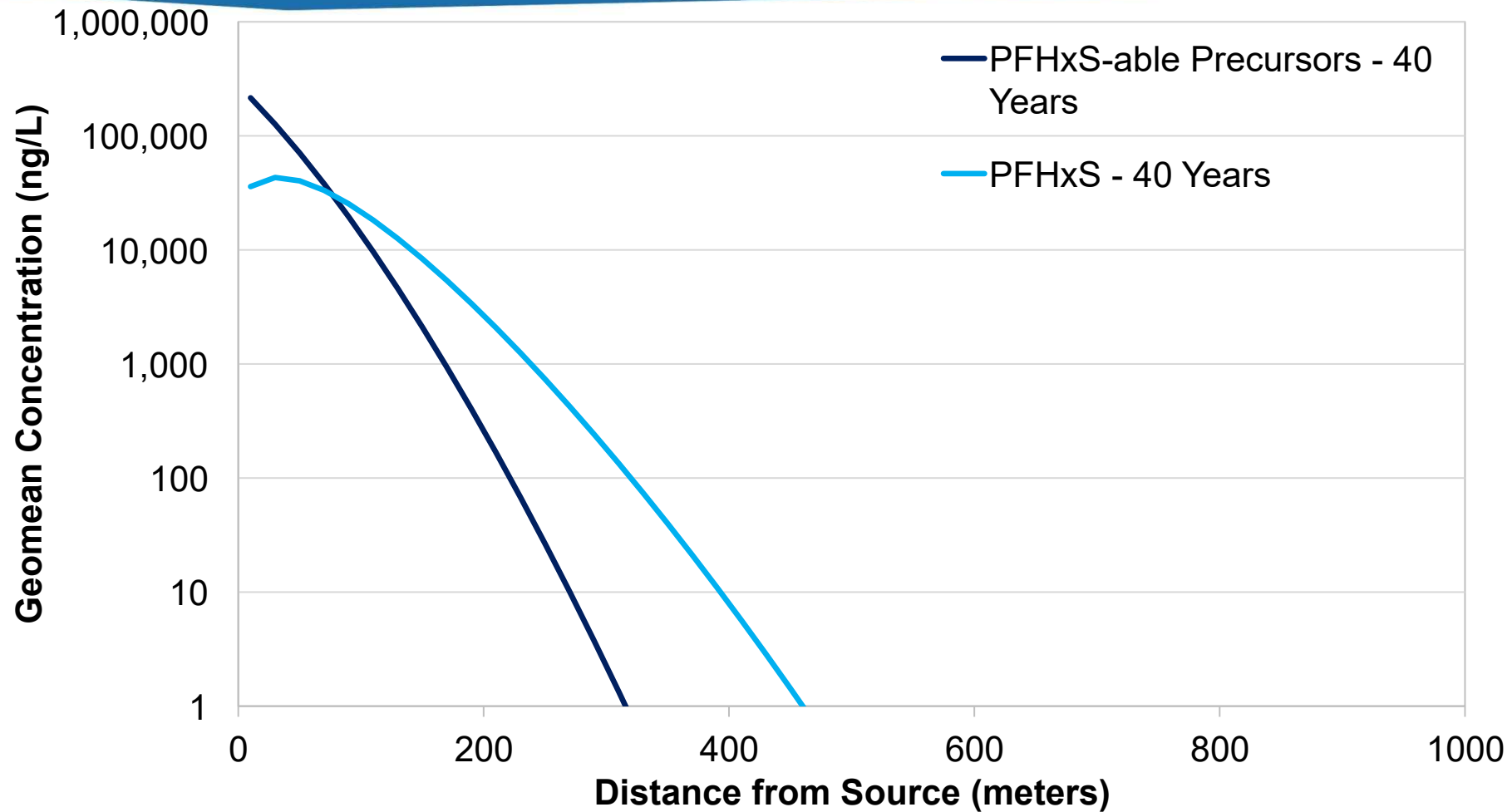


# Field Site PFHxS Model – Year 40

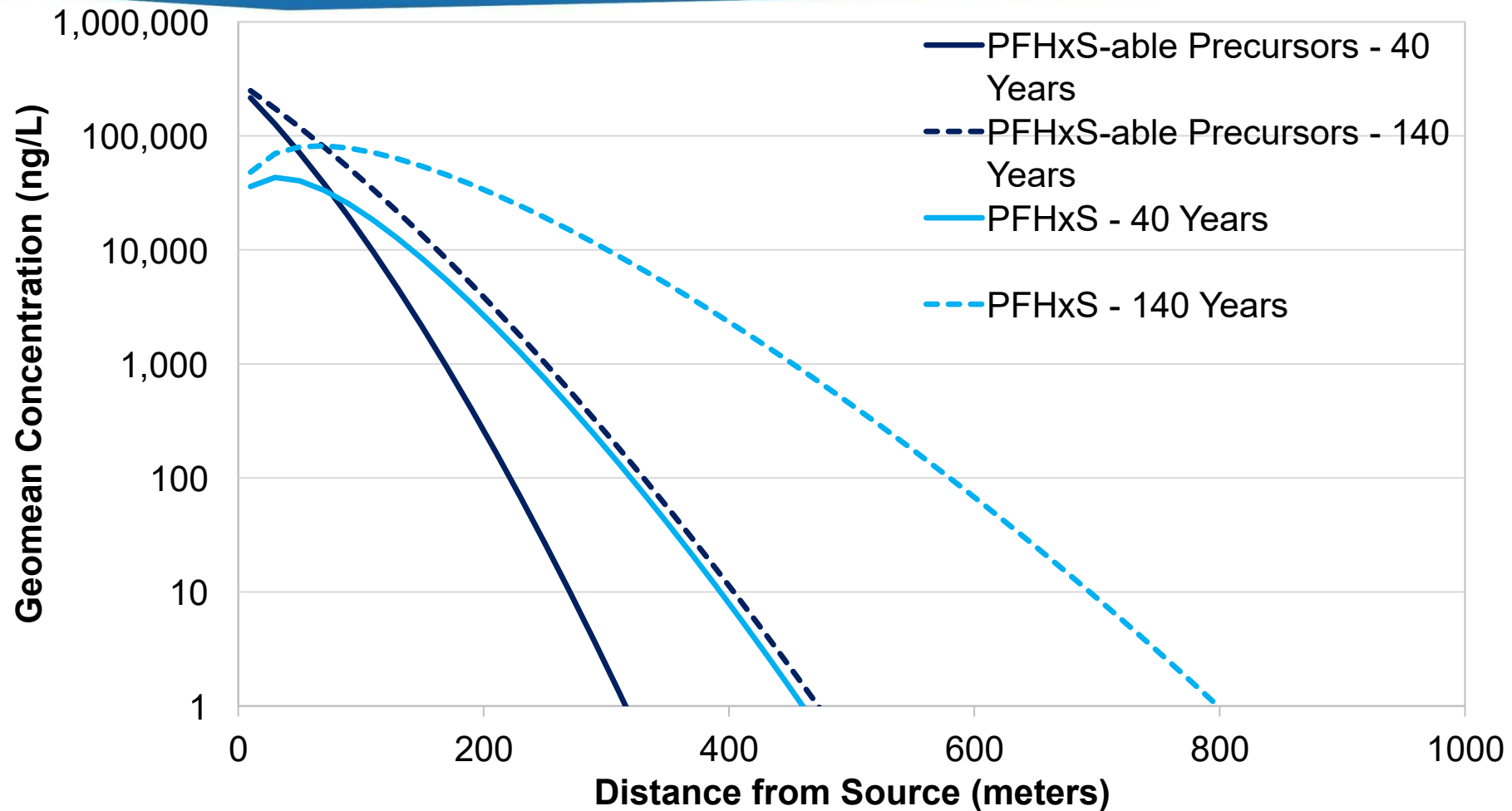


**PFHxS precursor transformation results in higher PFHxS concentrations and longer PFHxS plume**

# Field Site PFHxS Model – Year 40

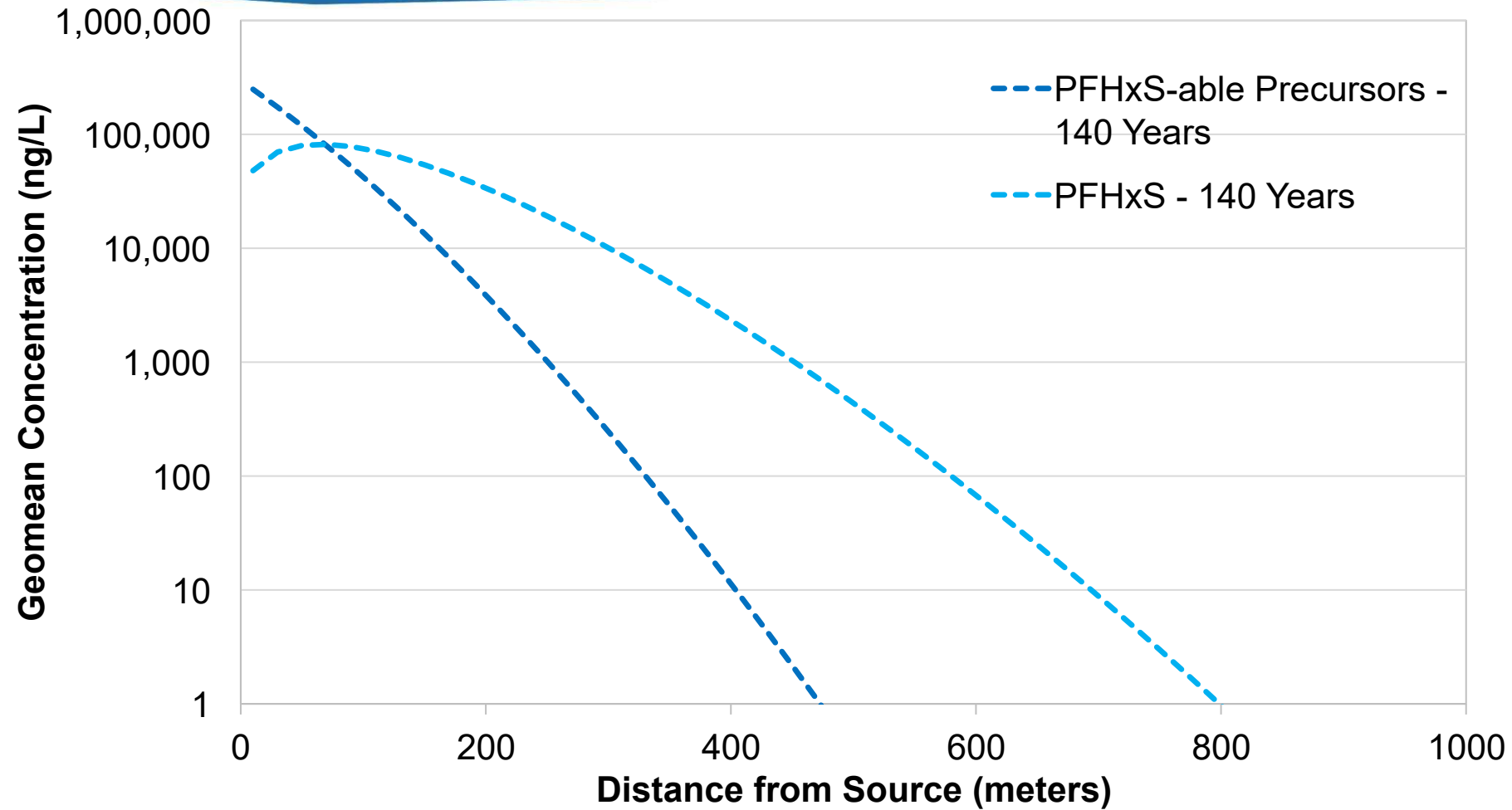


# Field Site PFHxS Model – Year 140

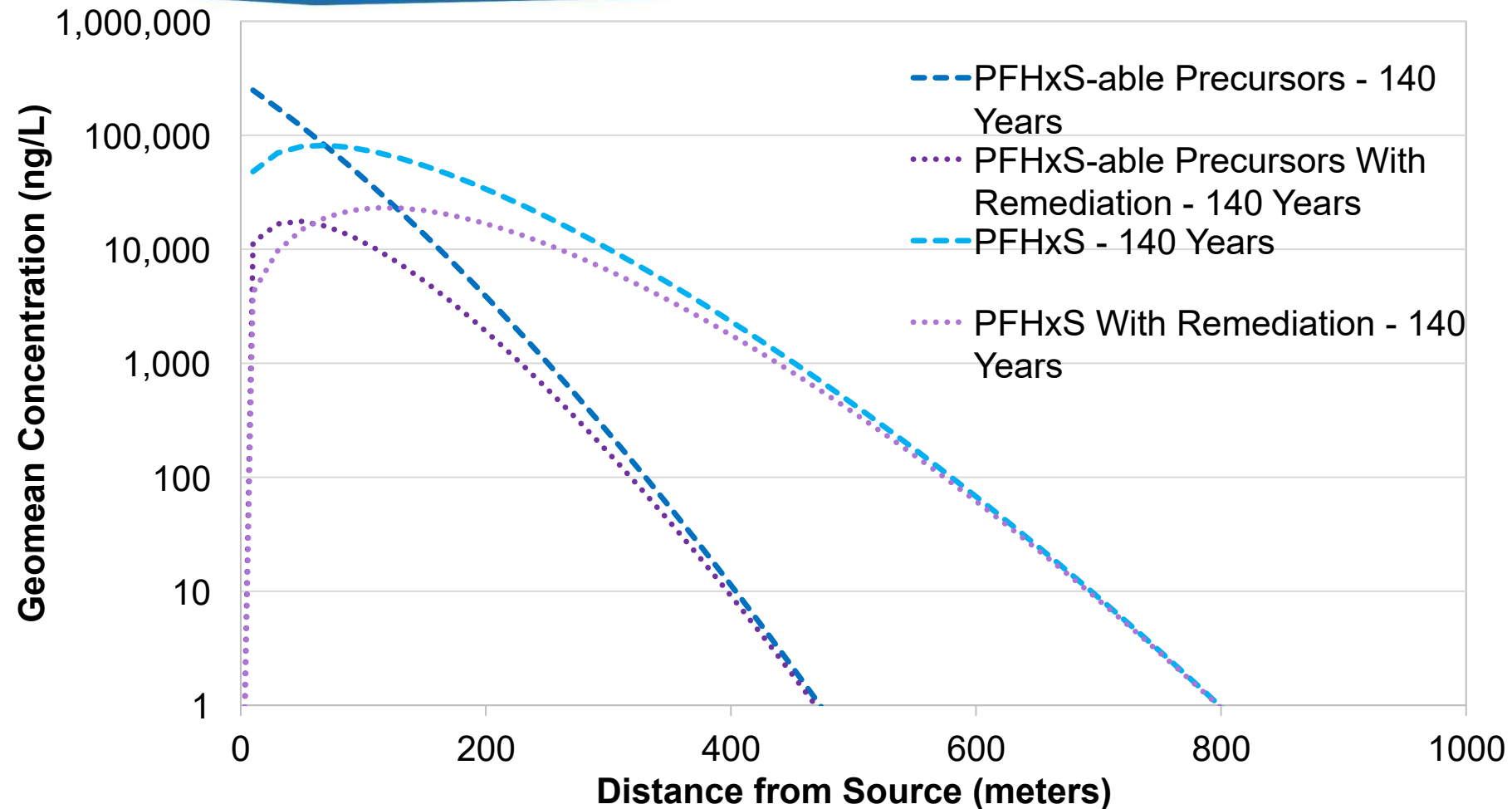


PFHxS-able precursor and PFHxS plumes still expanding due to continued release from source zone and migration of downgradient plume; PFHxS plume also expanding due to precursor transformation

# Field Site PFHxS Model – Year 140



# Field Site PFHxS Model – Year 140, With Source Remediation at Year 40



**Source concentrations decrease, but plumes persist and continue to expand downgradient due to continued migration of downgradient plume**

# Sensitivity Analysis Results

- › Key Fate and Transport Parameters:
  - › Retardation in low-k zones
  - › Precursor transformation rates
  - › Source mass at the time of release

| PFAS  | Parameter                       | Precursor Plume Length % Difference from Base Case | PFAA Plume Length % Difference from Base Case |
|-------|---------------------------------|----------------------------------------------------|-----------------------------------------------|
| PFOS  | PFOS Retardation in T-Zone      | ±0%                                                | ±8-13%                                        |
|       | PFOS Retardation in Low-k       | ±0%                                                | ±15-18%                                       |
|       | Precursor Retardation in T-Zone | ±3-6%                                              | ±0%                                           |
|       | Precursor Retardation in Low-k  | ±6%                                                | ±0%                                           |
|       | Precursor Yield in T-Zone       | ±0%                                                | ±0%                                           |
|       | Precursor Transformation Rate   | ±18-24%                                            | ±0%                                           |
| PFHxS | PFHxS Retardation in T-Zone     | ±0%                                                | ±7-9%                                         |
|       | PFHxS Retardation in Low-k      | ±0%                                                | ±16-21%                                       |
|       | Precursor Retardation in T-Zone | ±8-11%                                             | ±1-2%                                         |
|       | Precursor Retardation in Low-k  | ±14%                                               | ±2%                                           |
|       | Precursor Yield in T-Zone       | ±0%                                                | ±2%                                           |
|       | Precursor Transformation Rate   | ±5-6%                                              | ±2-3%                                         |

# Summary and Conclusions

- › Categorized potential precursors based on fluorinated carbon chain length
- › High-resolution field site precursor characterization
  - › Predominant precursor type = PFHxS-able precursors
  - › Wide range of precursors in source area soil and groundwater; shorter-chained, anionic precursors dominate mid-plume soil and groundwater
- › Modeled individual PFAAs and their grouped potential precursors using REMChlor-MD
  - › Retardation and precursor transformation rates are key parameters
  - › Impact of precursor transformation strongly influenced by concentration difference between precursors and terminal PFAAs; greatest for PFBS, PFHxS, and PFOA; no impact on PFOS
- › Conclusions are specific to the modeled field site
- › Manuscript of this work is currently in review
- › Next up = REMFluor model

