Examination of PFAS Present In ZVI Permeable Reactive Barrier: The Elizabeth City, NC, Case Study

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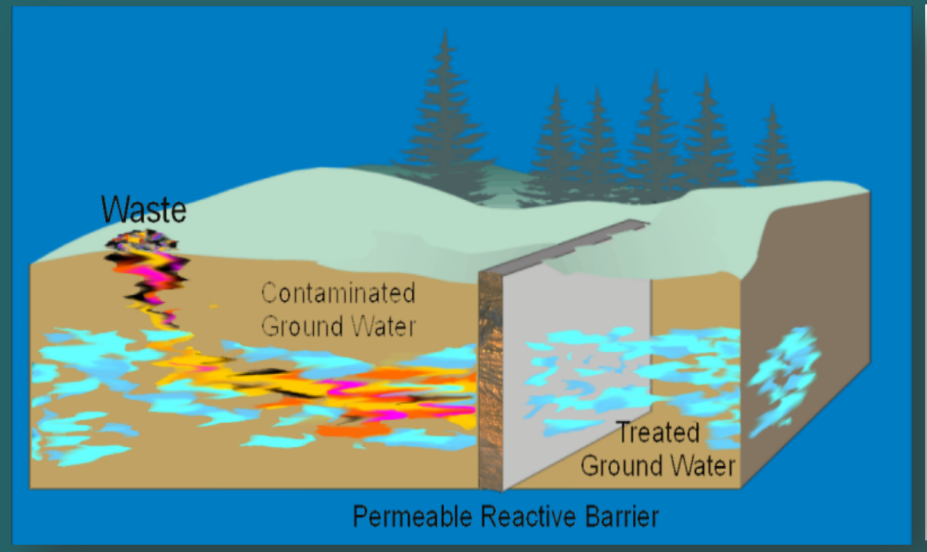
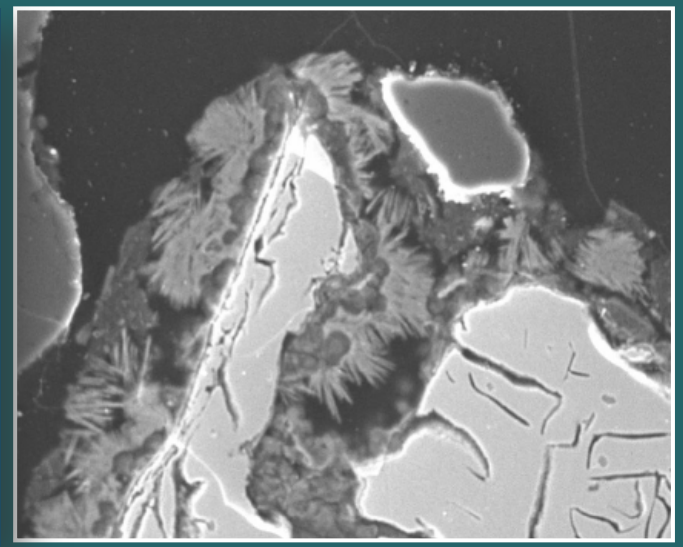
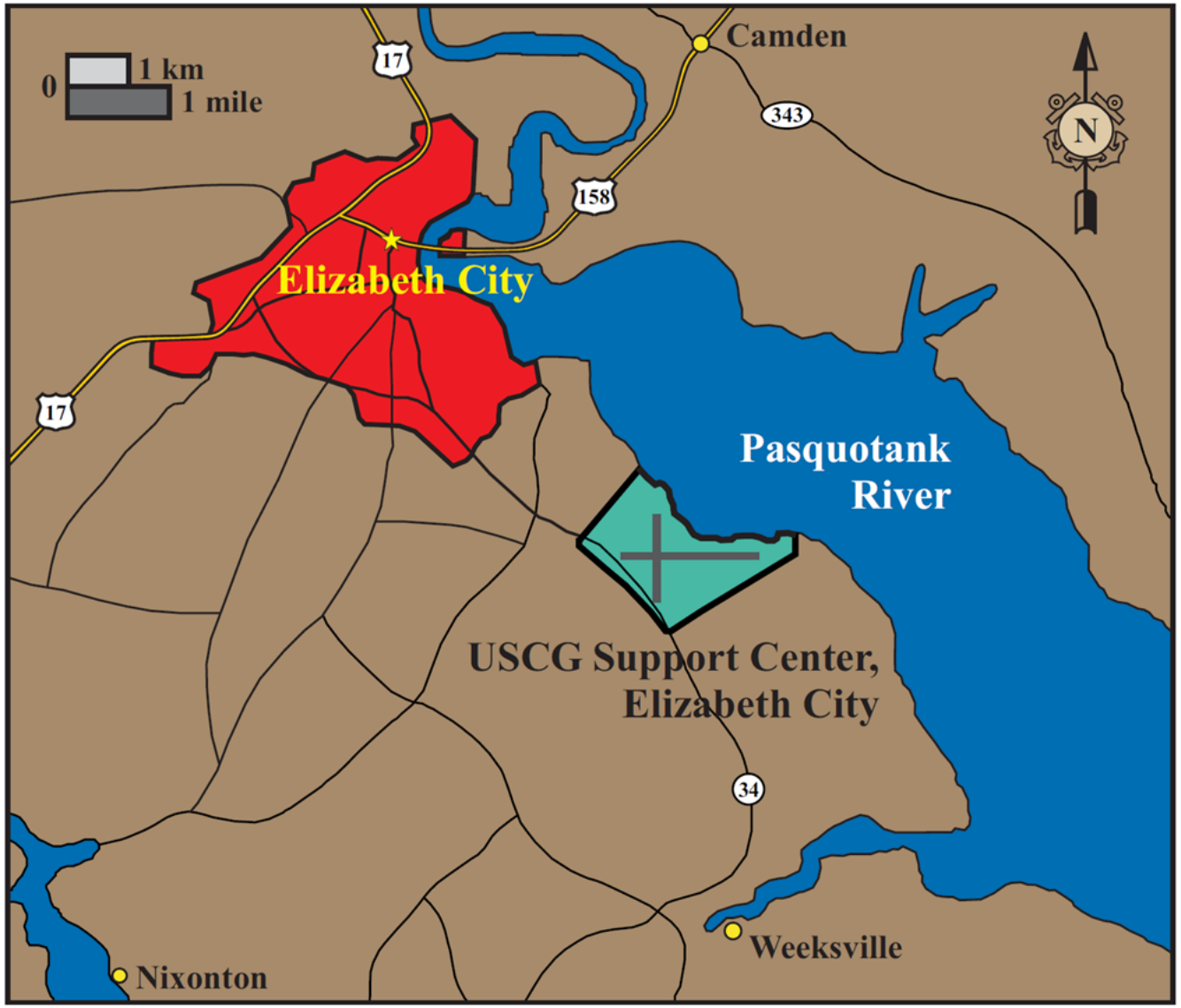




[1] EPA Office of Research and Development [2] EPA Region 5 [3] EPA Region 2

US Coast Guard Support Center, Elizabeth City, NC

- Groundwater impacted by hexavalent chromium and chlorinated solvents
- Former metal plating shop (possible PFAS source)
- Runway (possible AFFF source)



1993 1994 1996 2003 2019 2022

Puls, Powell, Paul labwork

Auger hole-
ZVI pilot
Cr to <10 µg/L
TCE <1 µg/L

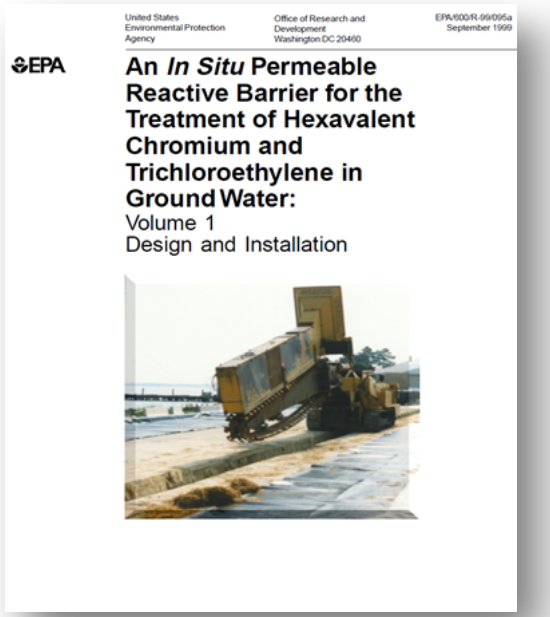
Full-scale installation

EPA & U Waterloo monitoring studies

EPA/USCG monitoring

EPA 1st PFAS sampling

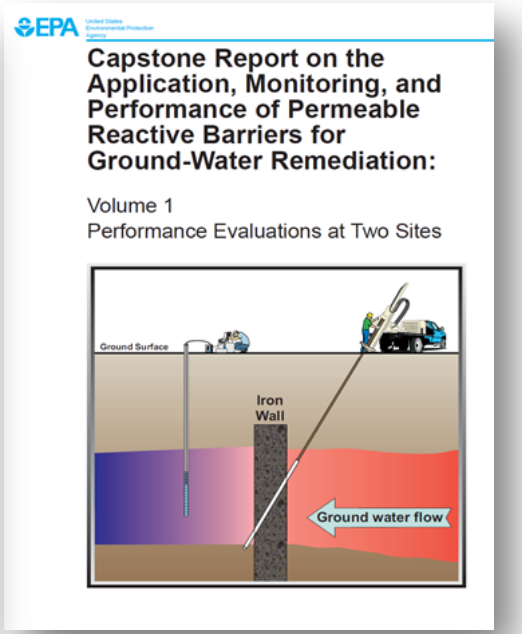
2023 EPA 2nd PFAS sampling


United States Environmental Protection Agency | Office of Research and Development Washington DC 20460 | EPA/600/R-99/095a September 1999

EPA

An *In Situ* Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water:
Volume 1
Design and Installation

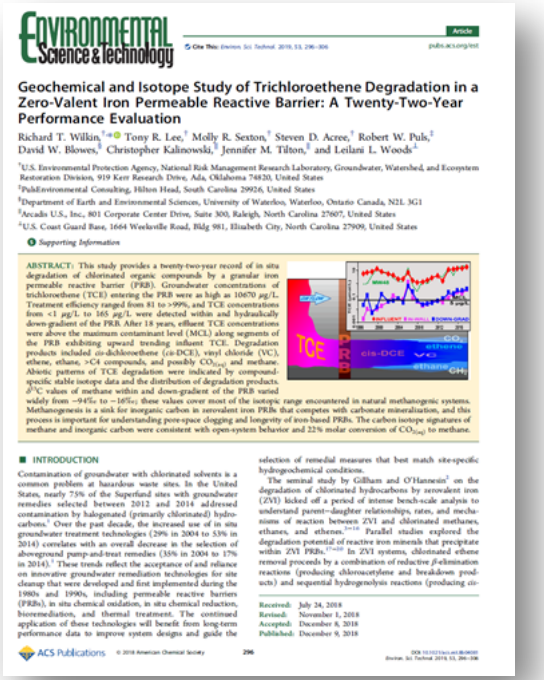
1999


EPA

Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation:

Volume 1
Performance Evaluations at Two Sites

2003

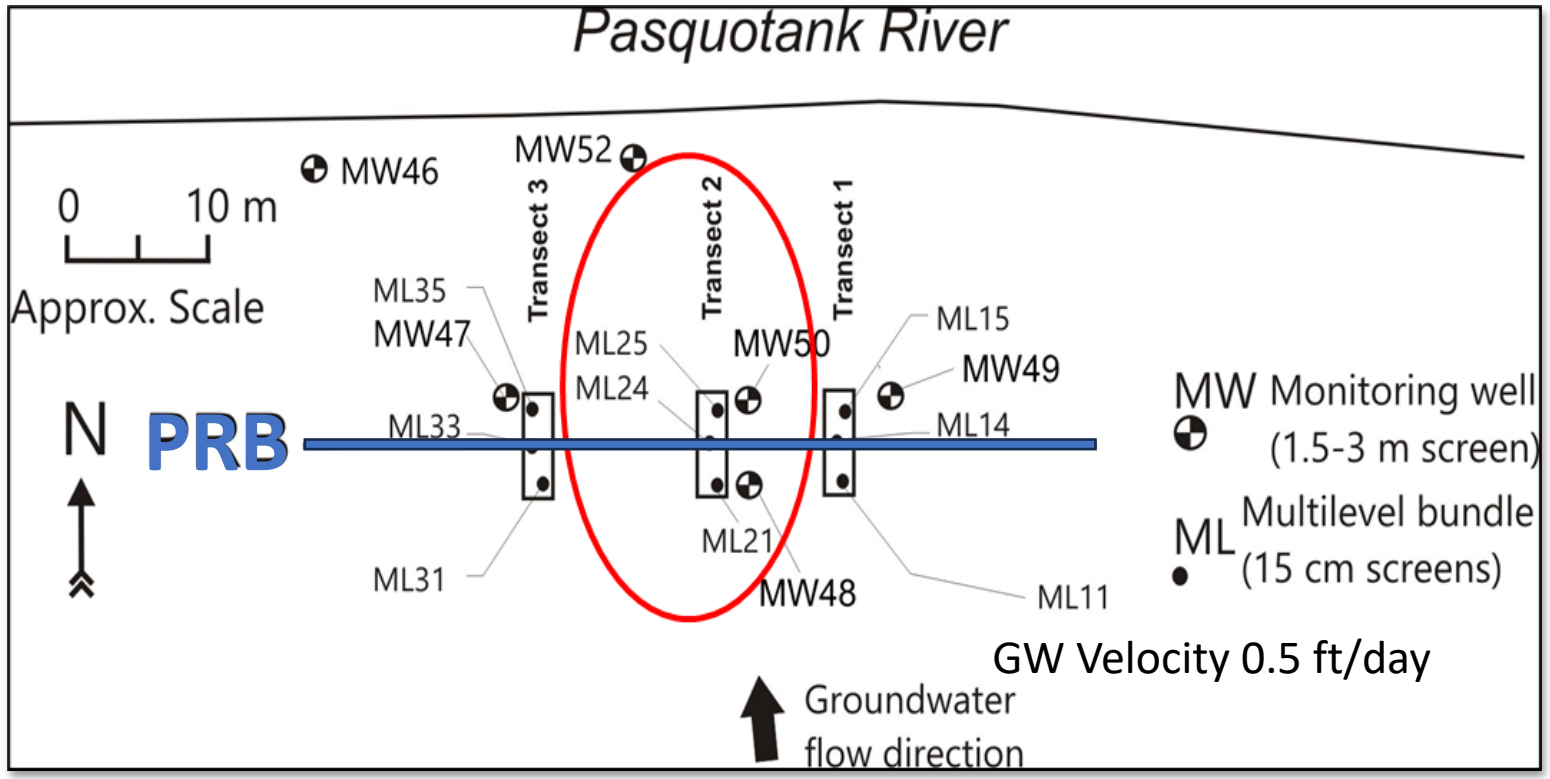

Environmental Science & Technology

Geochemical and Isotope Study of Trichloroethene Degradation in a Zero-Valent Iron Permeable Reactive Barrier: A Twenty-Two-Year Performance Evaluation

2019

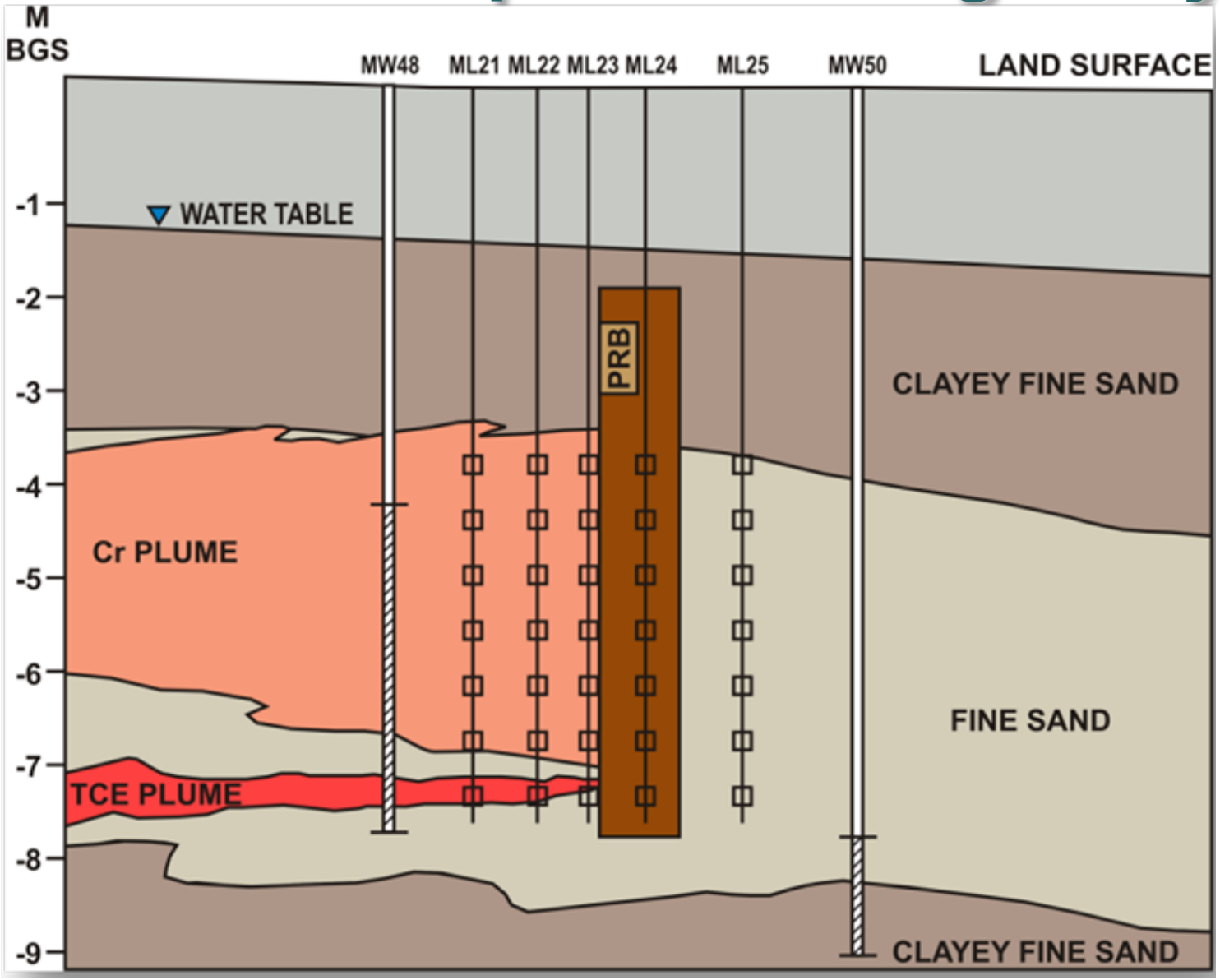
ZVI Permeable Reactive Barrier

- 450 tons of granular zero-valent iron keyed into an underlying low conductivity layer (22 ft BGS)
- 205 wells were installed for performance monitoring



- 27 years of PRB performance data for Cr(VI) and TCE
  - Chromate effectively remediated close to 3 decades
  - TCE is also treated but is still present along with cis-DCE and vinyl chloride

Vertical Aquifer Heterogeneity



- Well clusters ML21 (upgradient), ML24 (in wall), and ML25 (down gradient) were sampled for PFAS August 2022. The same well clusters along with 10 compliance wells and the Pasquotank river were sampled for PFAS July 2023.
- Each well cluster has seven wells with 15 cm screens ranging in depth of 4 to 7 meters deep

ZVI and PFAS Laboratory Studies

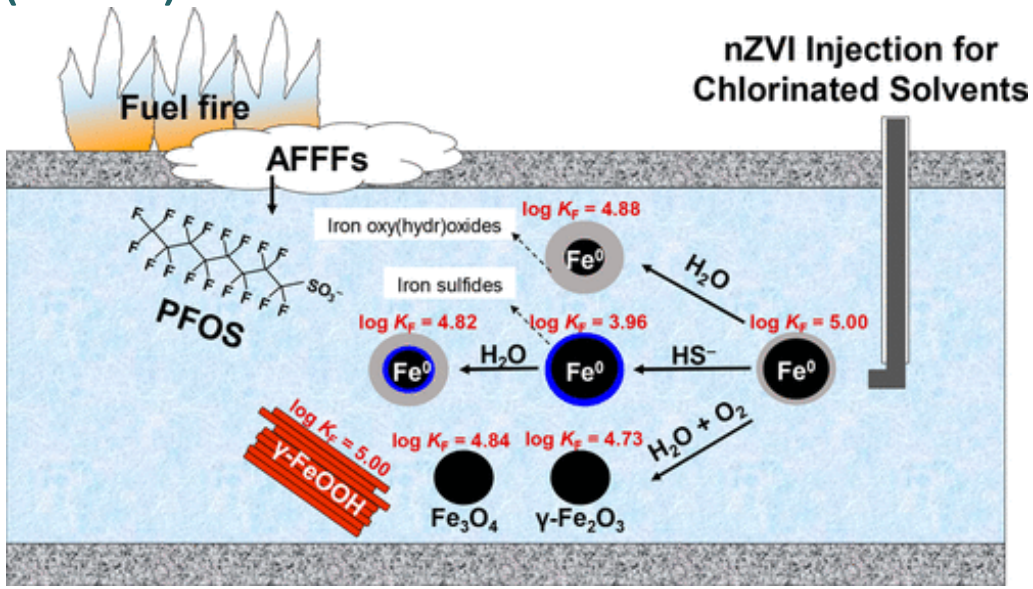
Zhang et al. (2018) found:

-Sorption to ZVI is 2-4 orders of magnitude higher than sediments, soils, and iron oxides.

- Aged (95 days) and fresh nZVI sorption are similar.

A DFT-based kinetic model by Blotevogel et al. (2018) indicated that PFAS removal by ZVI is likely due to adsorption and possibly decarboxylation.

Longer chain PFAS are more likely to adsorb to ZVI. Functional groups also play a role, with sulfonic acids adsorbing more than carboxylic acids. Zhang et al. (2018), Liu et al. (2020)

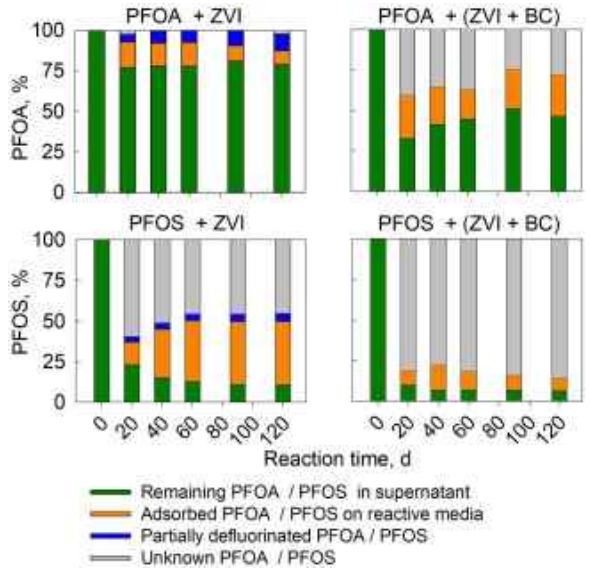


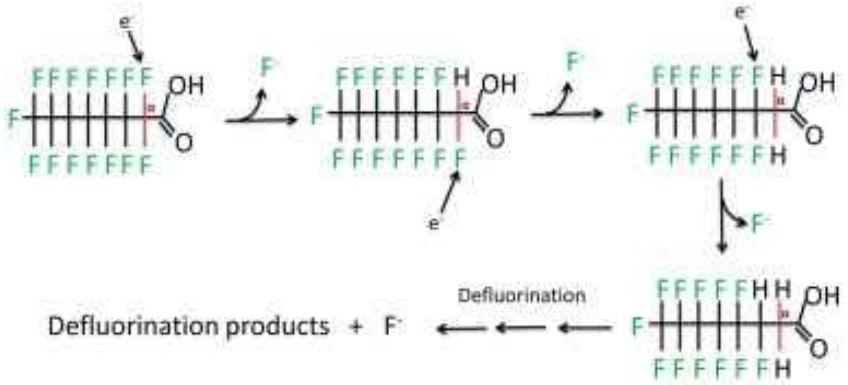
Zhang et al (2018)

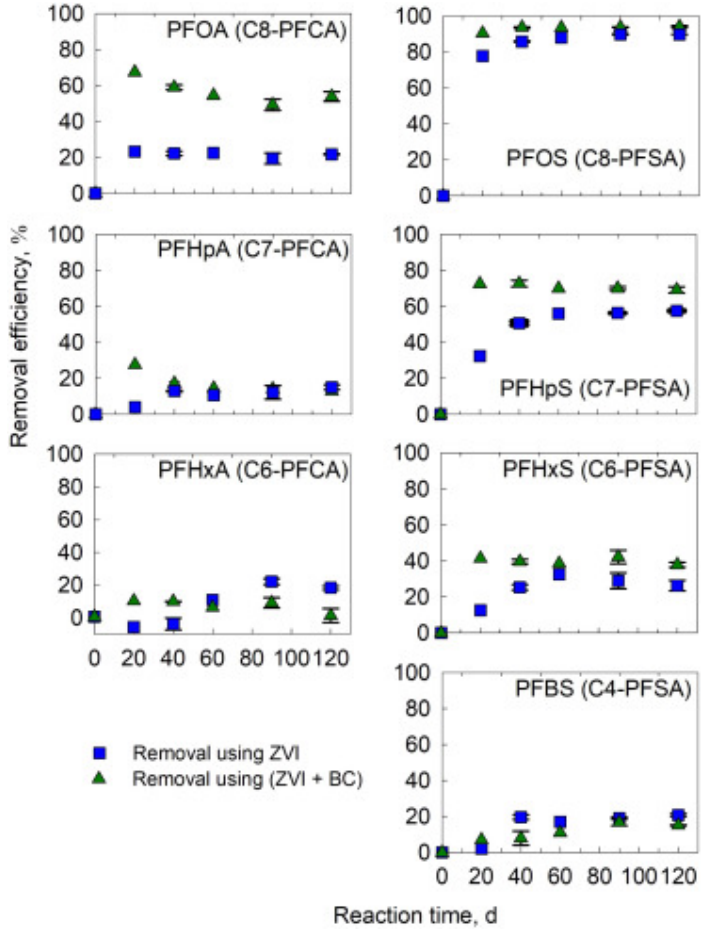
Modified ZVI and PFAS Laboratory Studies

Liu et al. (2020) created a medium using nZVI and biochar which had a removal efficiency of 17-94% for PFOA, PFHpA, PFOS, PFHpS, PFHxS, and PFBS.

Inorganic fluoride was also detected indicating defluorination. This accounted for 5-10% of PFAS removal.







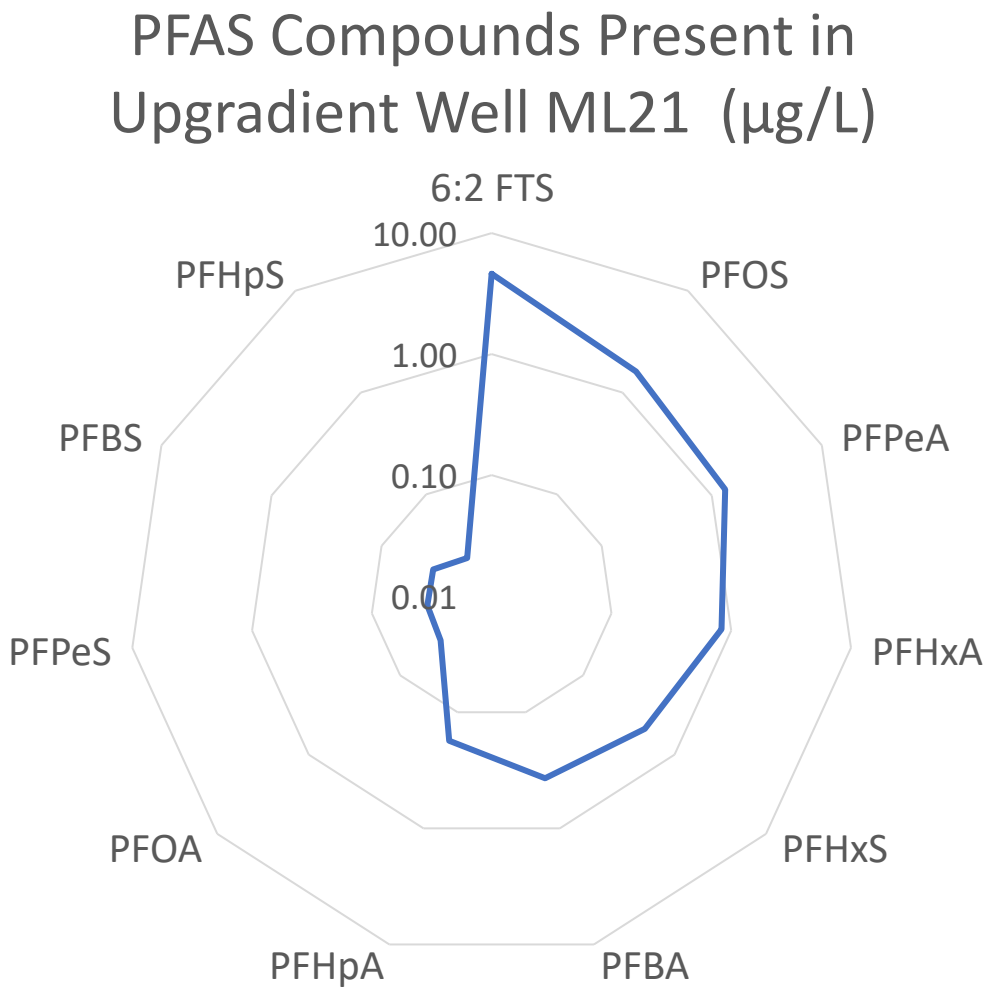
This Study: analytes and methods

- PFAS – EPA Method 8327 (Direct Injection Ultra High-Performance Liquid Chromatography (UHPLC)-Tandem Mass Spectrometry (MS/MS))
- Total Organic Fluorine - Combustion Ion Chromatography (CIC) EPA Method 1621
- Inorganic Fluoride - Dionex ICS-2100 Ion Chromatography

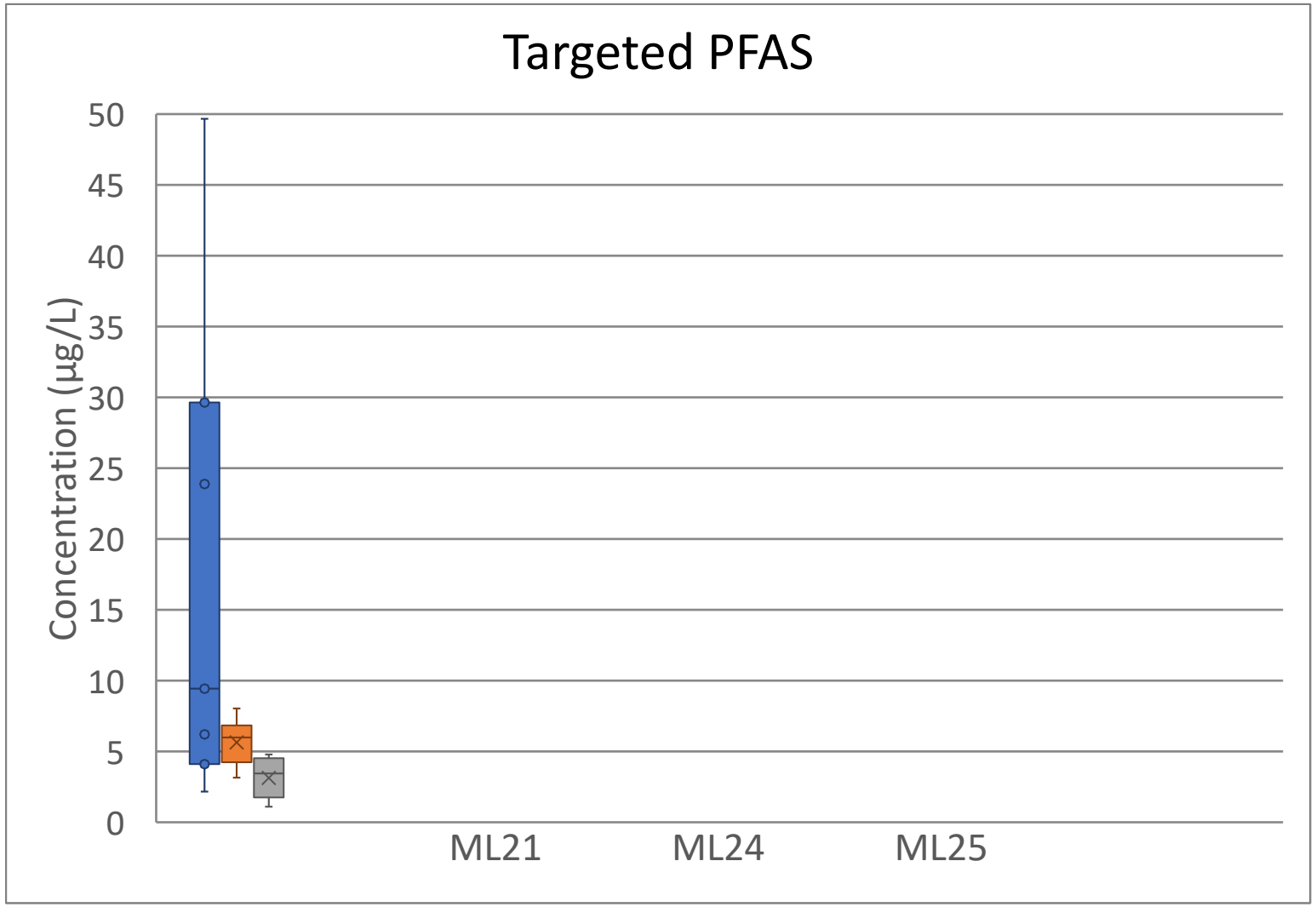
Metals, Anions, Dissolved Gases, Dissolved Inorganic and Organic Carbon, Volatile Organic Compounds, Geochemical Parameters

PFAS Compounds Present

Compound	Abbreviation	Formula	Grouping
Perfluorobutanoic acid	PFBA	$C_4HF_7O_2$	Short Chain PFCA
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	Short Chain PFCA
Perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	Short Chain PFCA
Perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	Short Chain PFCA
Perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	Long Chain PFCA
Perfluorobutanesulfonate	PFBS	$C_4HF_9O_3S$	Short Chain PFSA
Perfluoropentanesulfonic acid	PFPeS	$C_5HF_{11}O_3S$	Short Chain PFSA
Perfluorohexanesulfonate	PFHxS	$C_6HF_{13}O_3S$	Long Chain PFSA
Perfluoroheptanesulfonic acid	PFHpS	$C_7HF_{15}O_3S$	Long Chain PFSA
Perfluorooctanesulfonate	PFOS	$C_8HF_{17}O_3S$	Long Chain PFSA
Fluorotelomer sulphonic acid 6:2	6:2 FTS	$C_8H_5F_{13}O_3S$	Long Chain PFSA



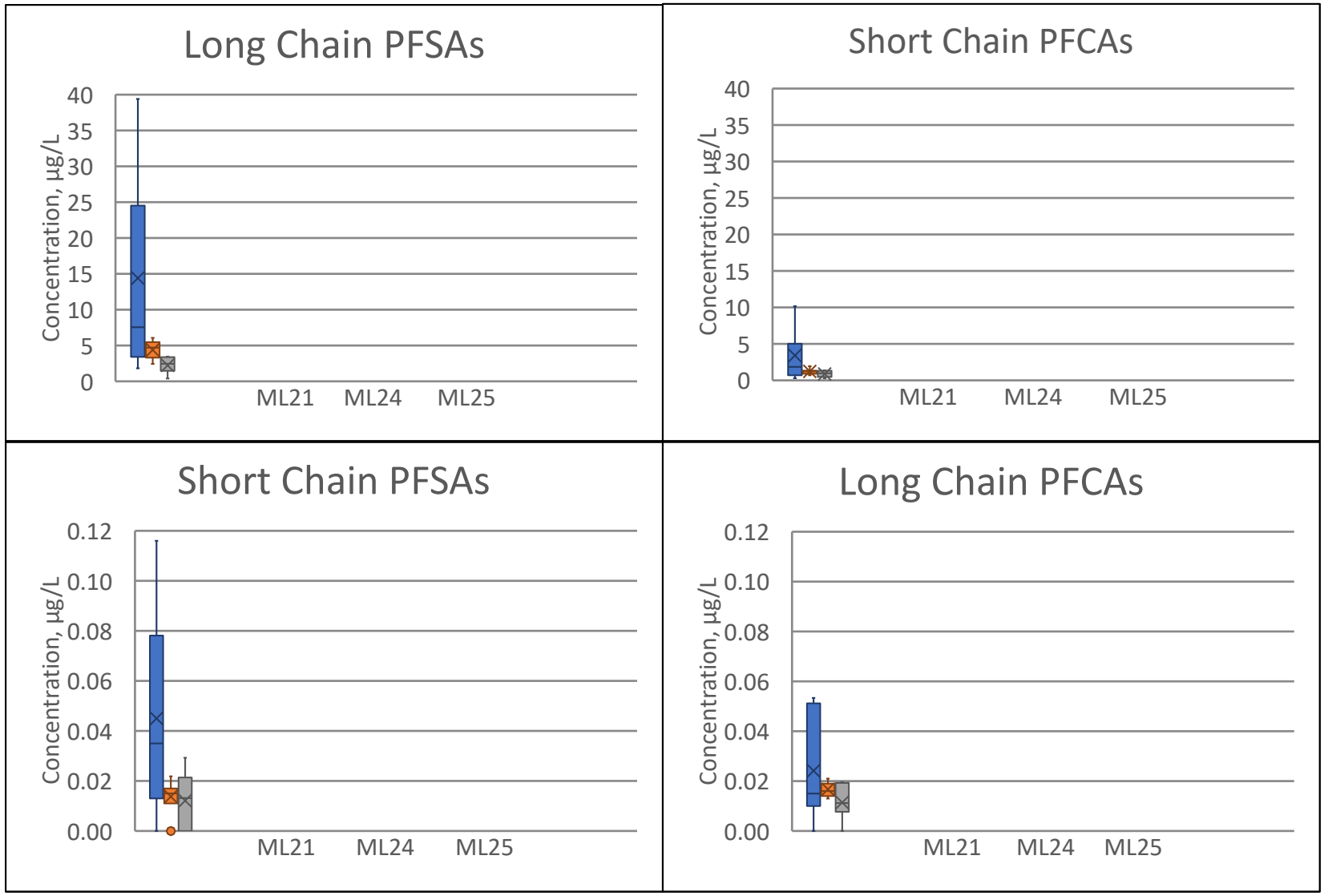
Average ΣPFAS Concentrations - 2023



ML21 – Upgradient
ML24 – In Wall
ML25 – Downgradient

- PFAS is decreasing across the PRB; ~80% removal
- The PRB is well mixed, and the effluent is relatively homogeneous

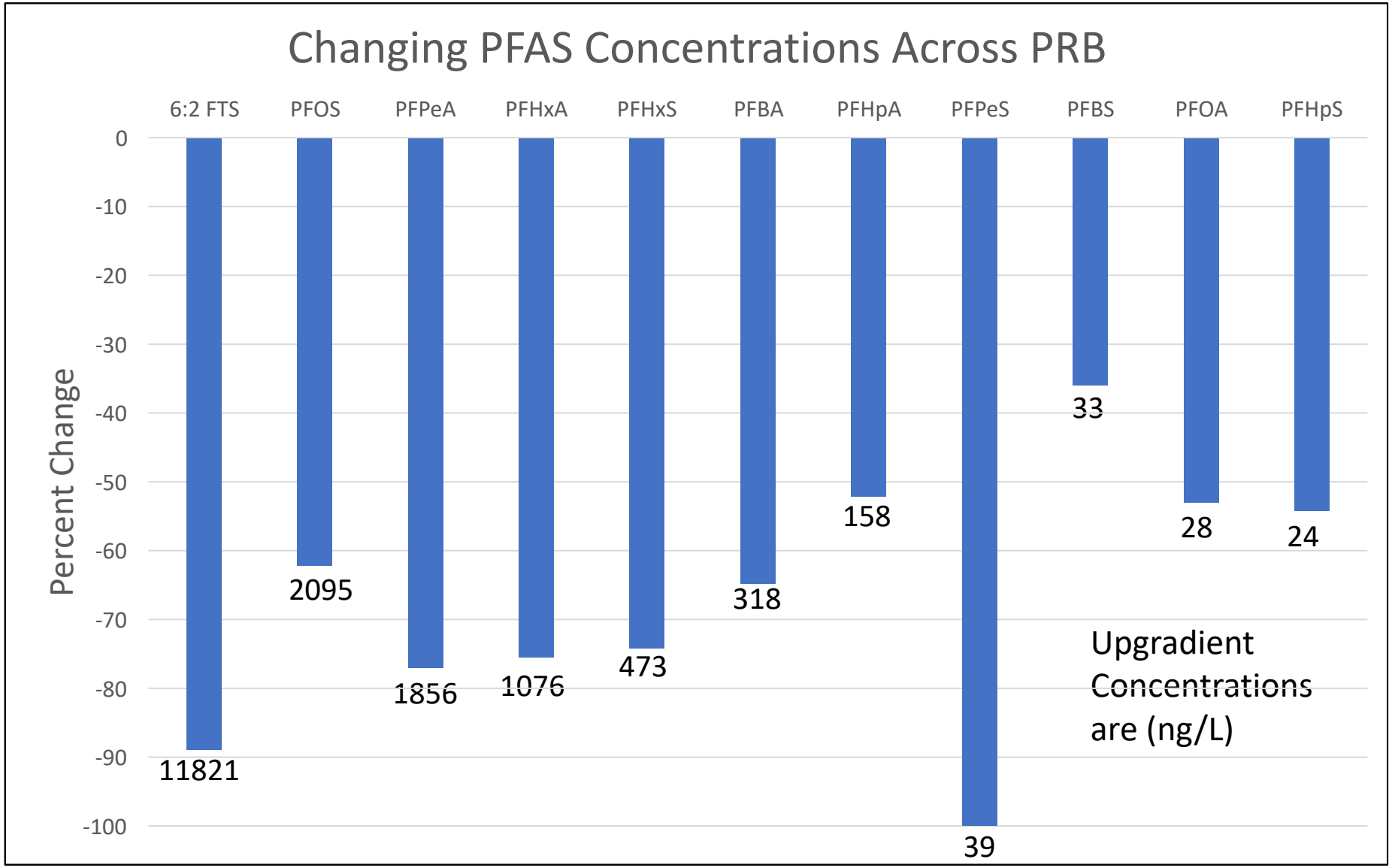
PFAS Groupings



ML21 – Upgradient
ML24 – In Wall
ML25 – Downgradient

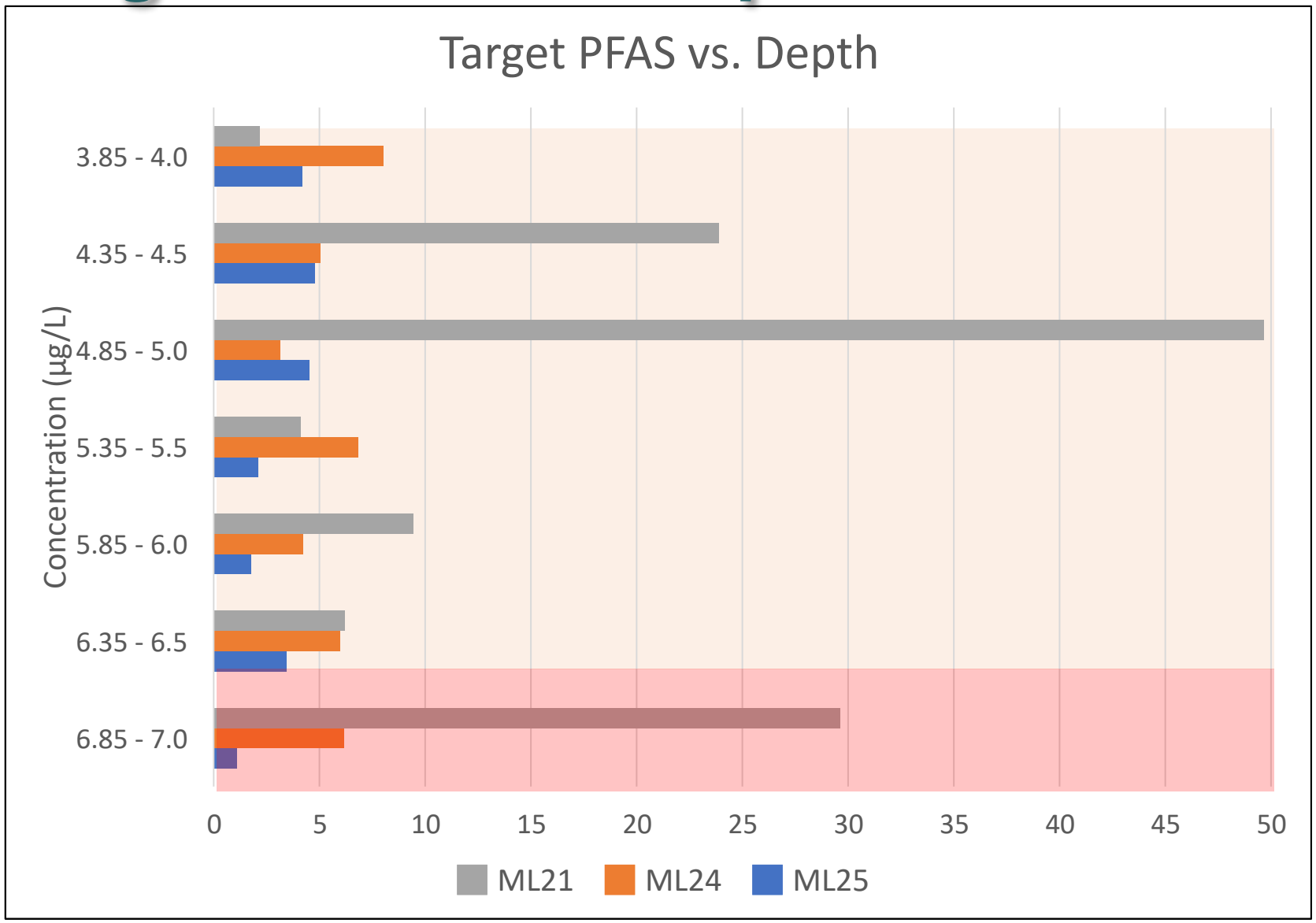
Long Chain Polyfluoroalkyl Sulfonic Acids and Short Chain Polyfluoroalkyl Carboxylic Acids are the most abundant.

Decreasing PFAS Concentrations



PRB removal mechanism does not appear to favor a particular type of PFAS

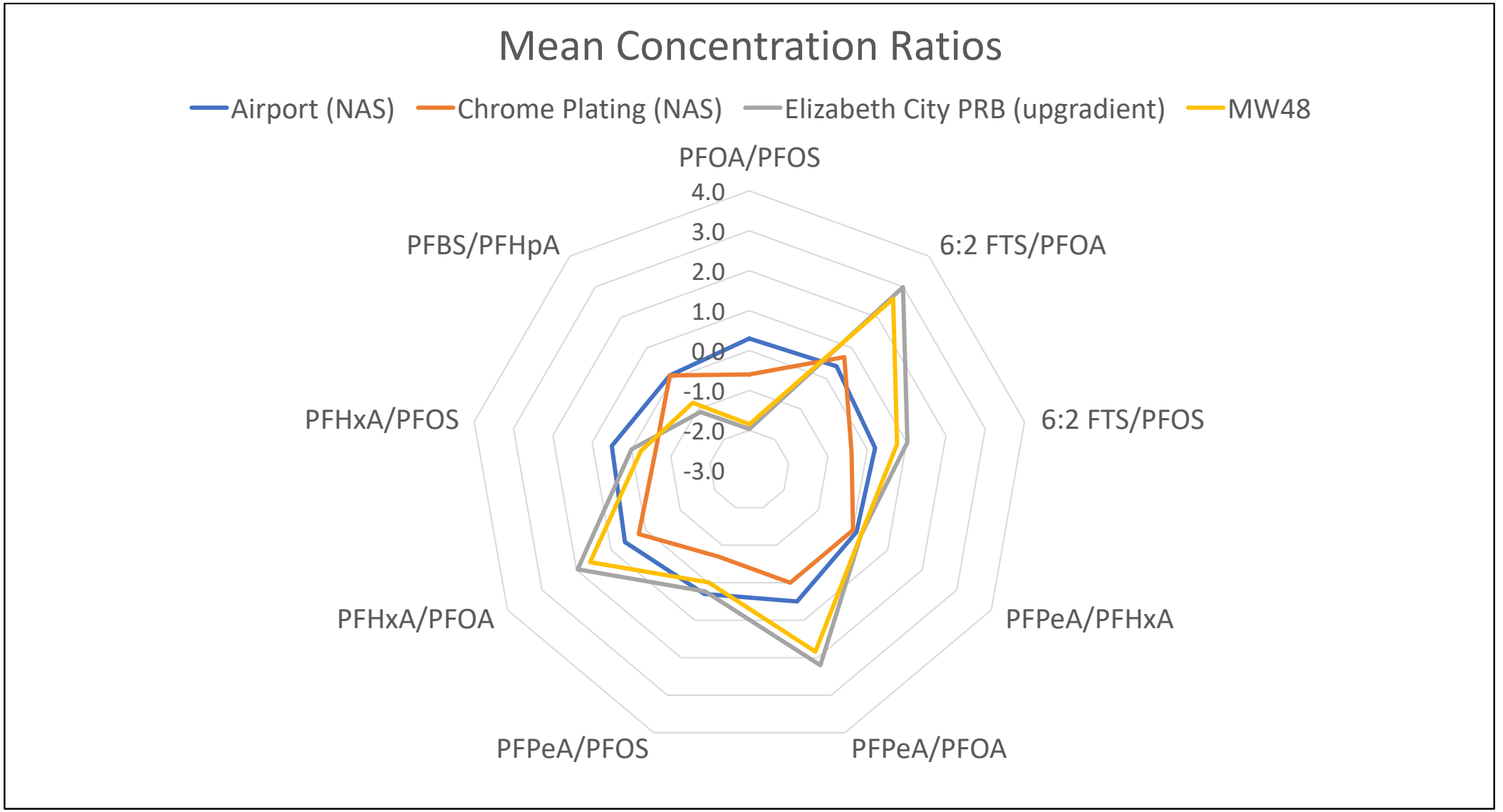
Target ΣPFAS vs. Depth - 2023



PFAS concentrations are highest upgradient of the PRB between 4.35 and 5.0 meters deep and 6.85-7.0 meters deep.

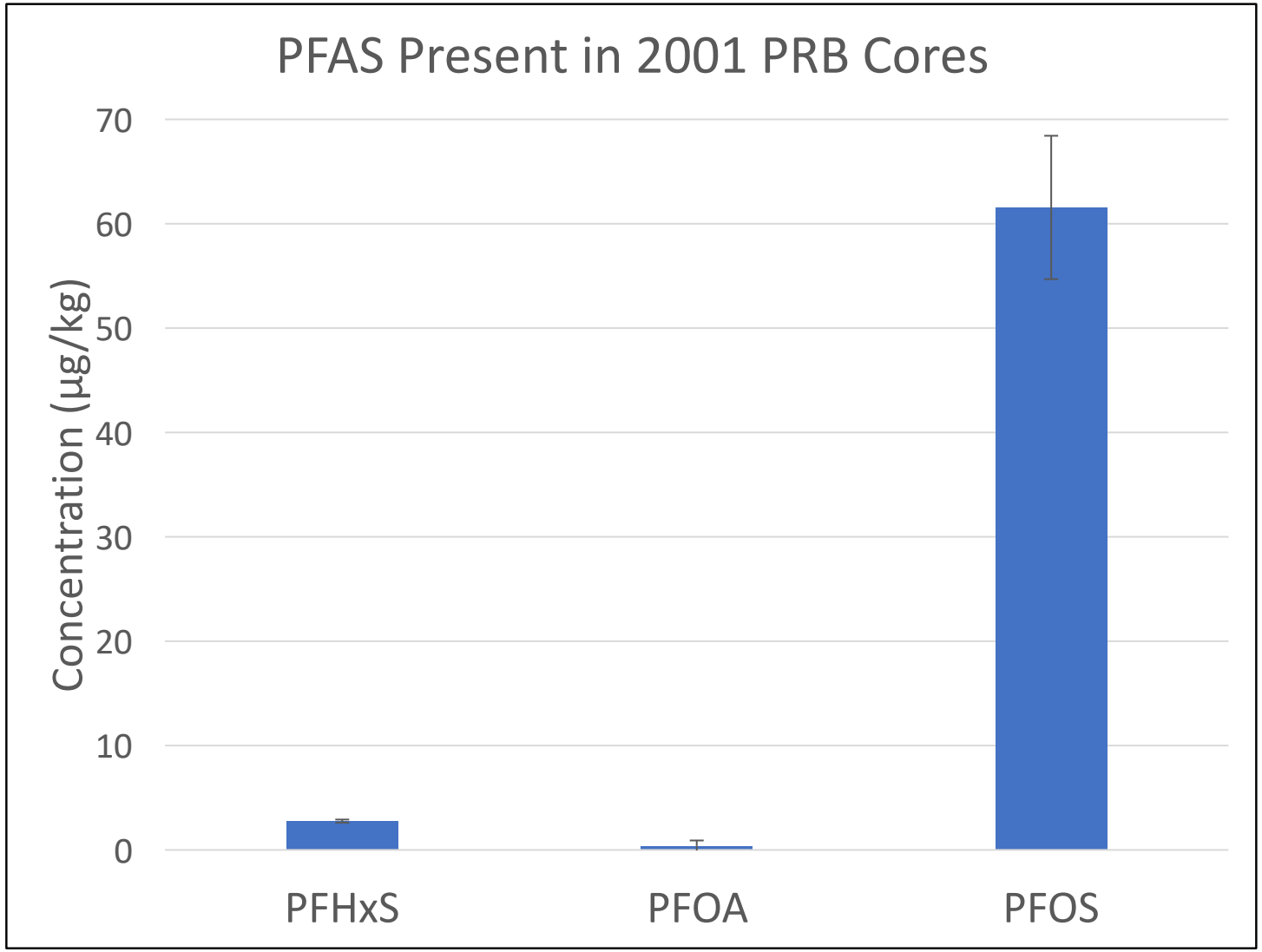
ML21 – Upgradient
ML24 – In Wall
ML25 – Downgradient

Possible Sources of PFAS



National Academies of Sciences, Engineering, and Medicine. 2023. PFAS Source Differentiation Guide for Airports. Washington, DC: The National Academies Press. https://doi.org/10.17226/27164.

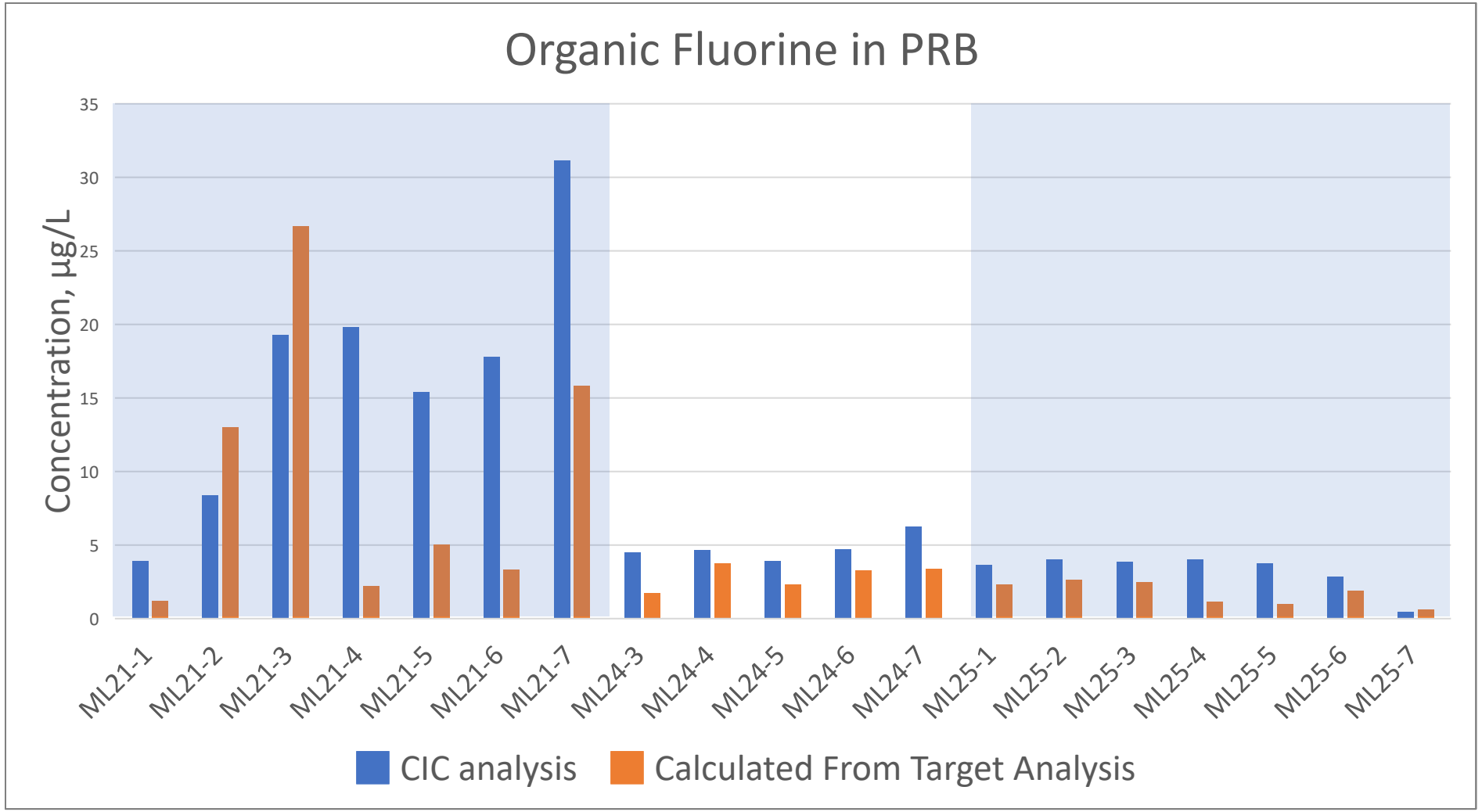
Historic In Wall ZVI Solids



- Three samples taken in 2001 from approximately 5-7 m deep
- PFOS dominant with minor amounts of PFHxS and PFOA

➢ Results indicate 6:2 FTS likely come from a modern AFFF product. The former metal plating shop used a PFOS mist suppressant.

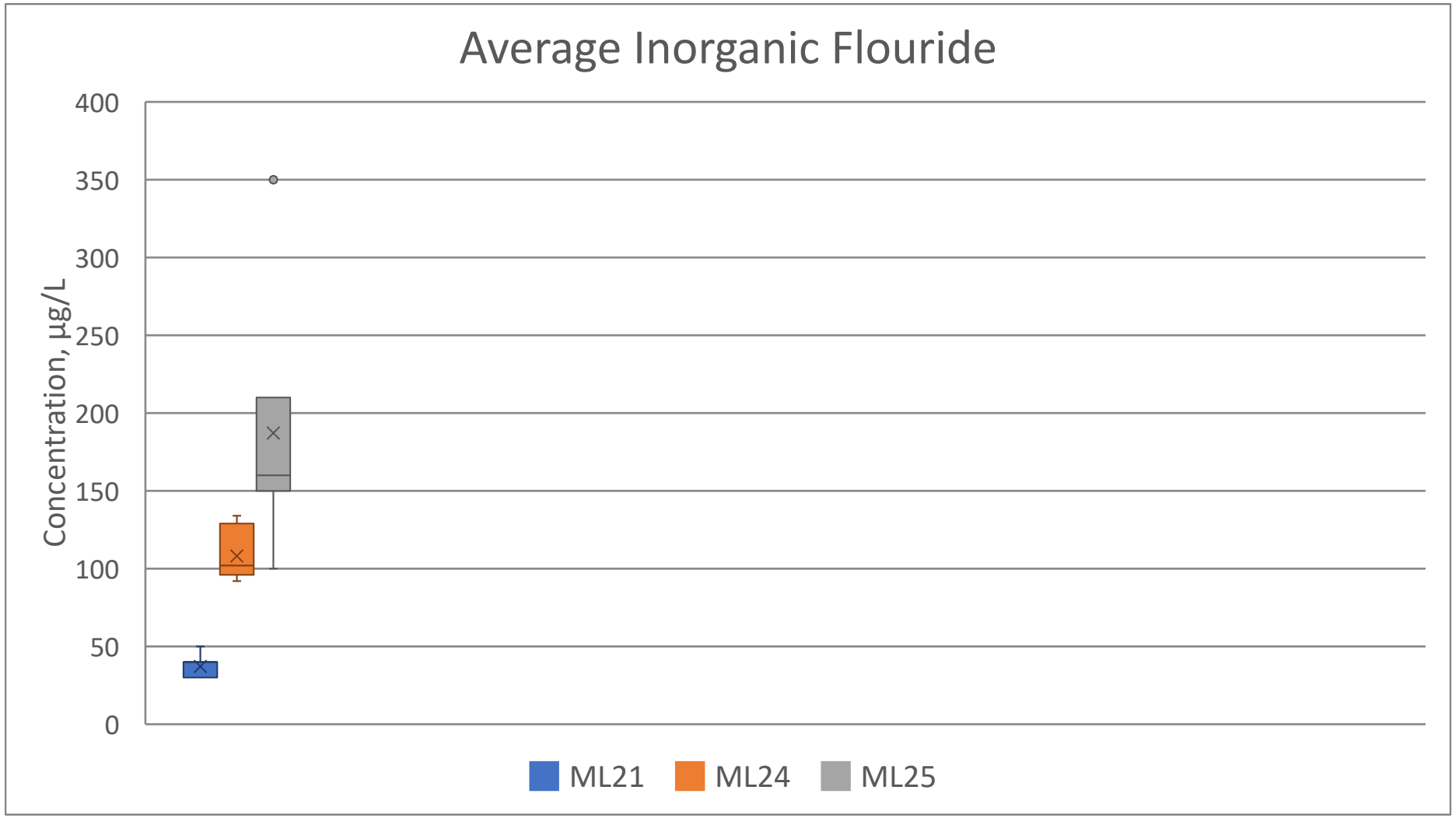
Total Organic Fluorine - 2023



ML21 – Upgradient
ML24 – In Wall
ML25 – Downgradient

~40% is not accounted for in the targeted analysis!

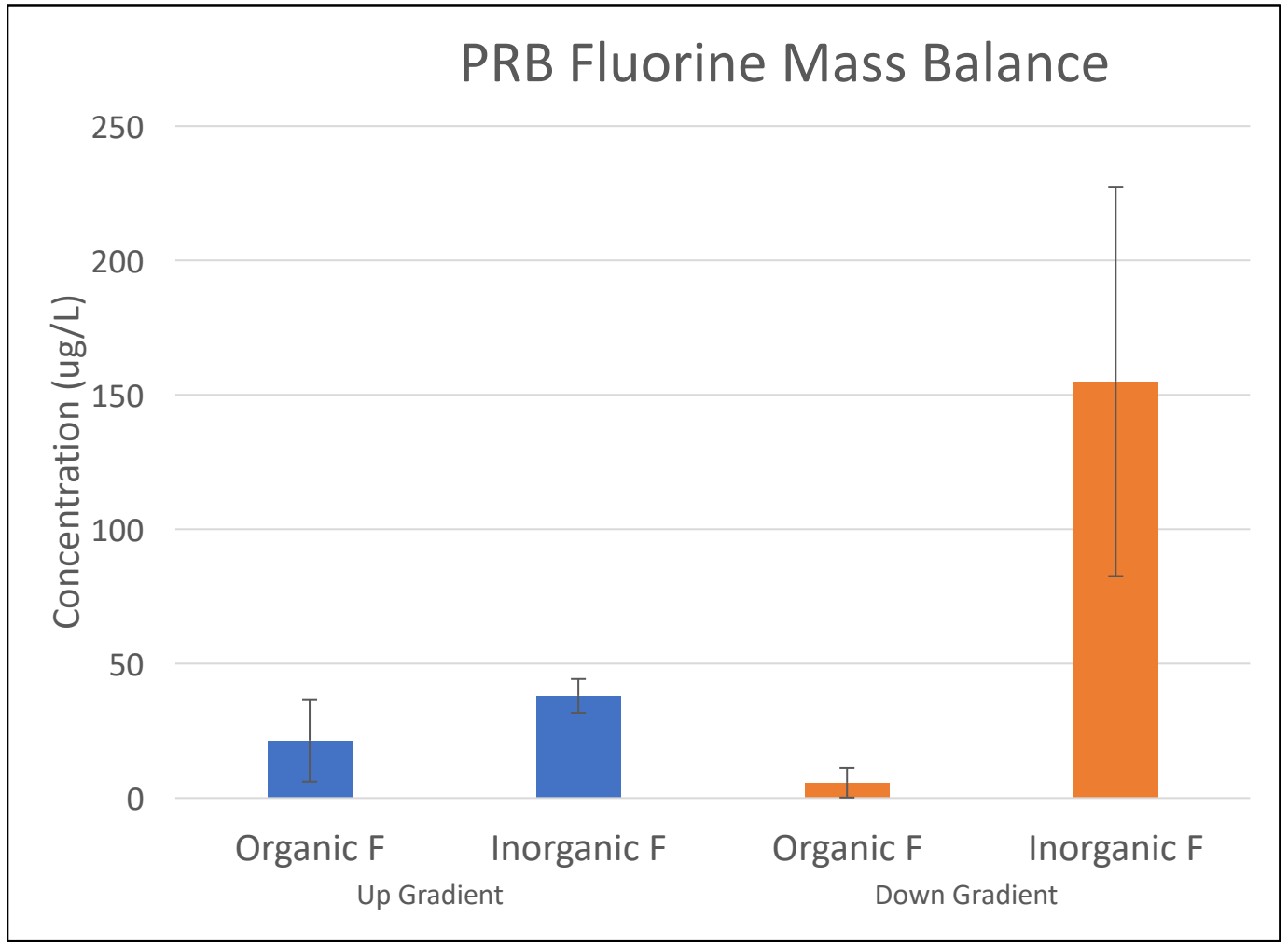
Inorganic Fluoride



ML21 – Upgradient
ML24 – In Wall
ML25 – Downgradient

Average inorganic fluoride increased by ~150 µg/L

Mass Balance Estimates



- Total organic fluorine and inorganic fluoride were tested
- Inorganic fluoride is increasing across the PRB at a rate 11 times higher than organic fluorine is being lost
- These observations suggest that the PRB may be driving a defluorination reaction

Conclusions

A 27-year-old PRB was able to reduce PFAS concentrations by ~80% (input ΣPFAS ~10 ppb) without any PFAS-specific design elements. This demonstrates:

- ZVI PRBs can be an effective method for partially removing PFAS contamination from groundwater along with co-contaminants such as chlorinated solvents and chromate.
- Existing PRBs may already be reducing PFAS contamination at other sites. This is relevant due to the prevalence of PFAS contamination.
- The presence of inorganic fluoride downgradient of the PRB could be indicative of an anaerobic defluorination reaction facilitated by the ZVI. Considering the age of this PRB there could be other factors at play other than the ZVI, for example, iron corrosion/or reaction products.

Questions