Co-metabolic Transformation and Treatment of PFAA Precursors in PFAS-Impacted Soils and Aquifer Sediments (ER22-3312)

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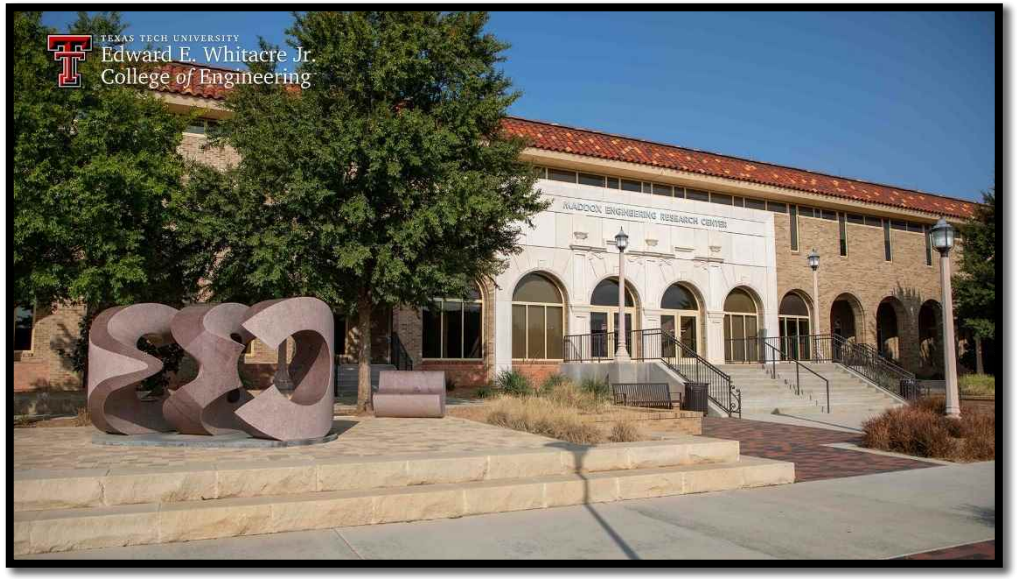


Research Team

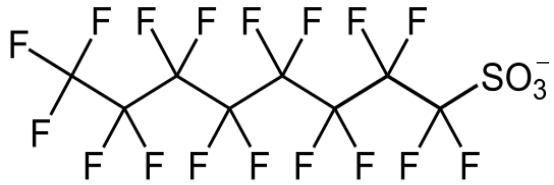
- *APTIM Federal Services LLC.*
  - *Dr. Paul Hatzinger (PI)*
  - *Rachael Rezes*

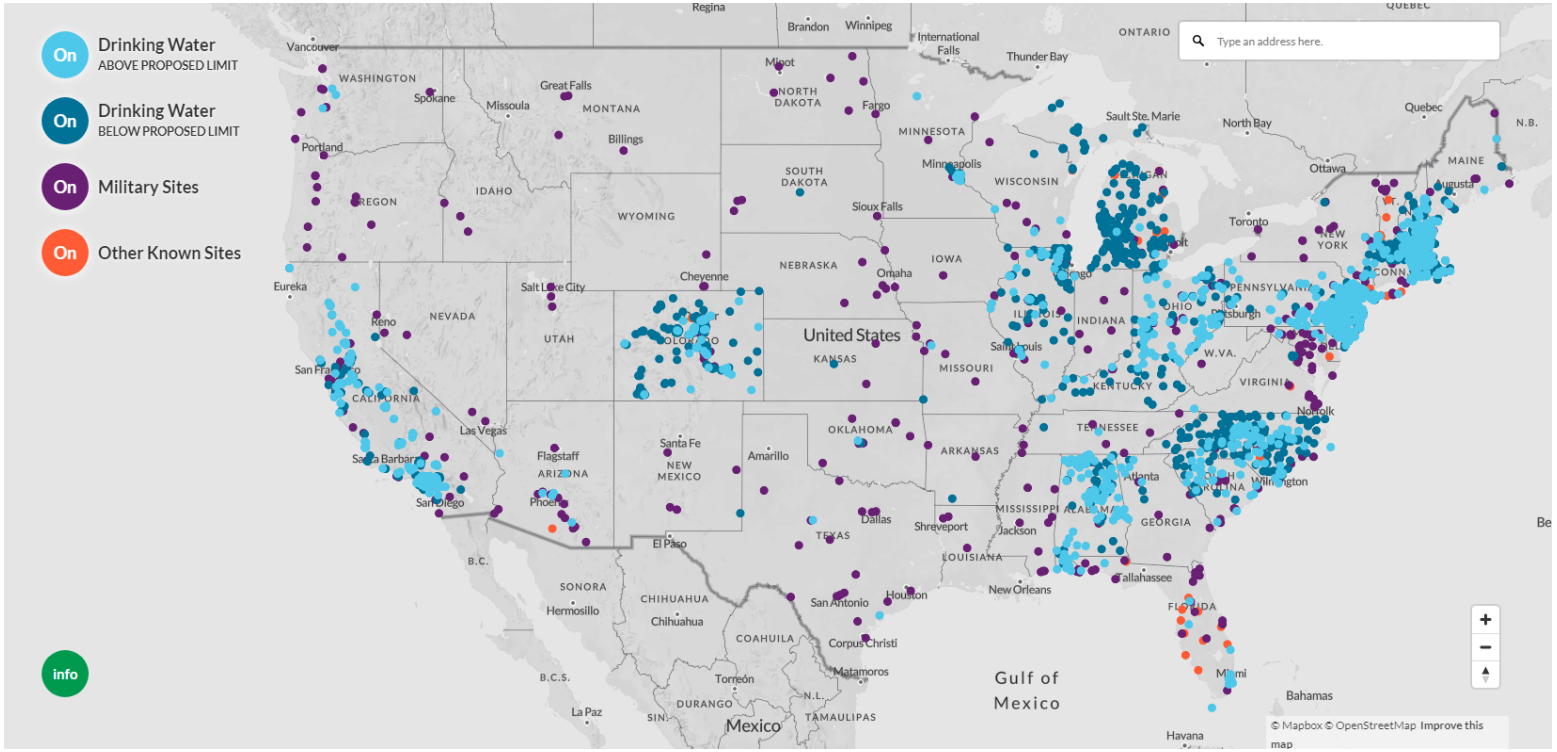
Texas Tech University
  - *Dr. Andrew Jackson*
  - *Dr. Jennifer Guelfo*
  - *Jessica LaFond*

Introduction and Project Overview

What is PFAS and why is it a problem?

- Per and poly fluoroalkyl substances
- Class of over 12000 compounds
- Fluorinated carbon backbone
- Functional heads +/-/+-
- Fire-fighting activities released large quantities into groundwater
- Why do we care? -> Toxic low concentrations, EPA just released new proposed drinking water standard
- Very recalcitrant





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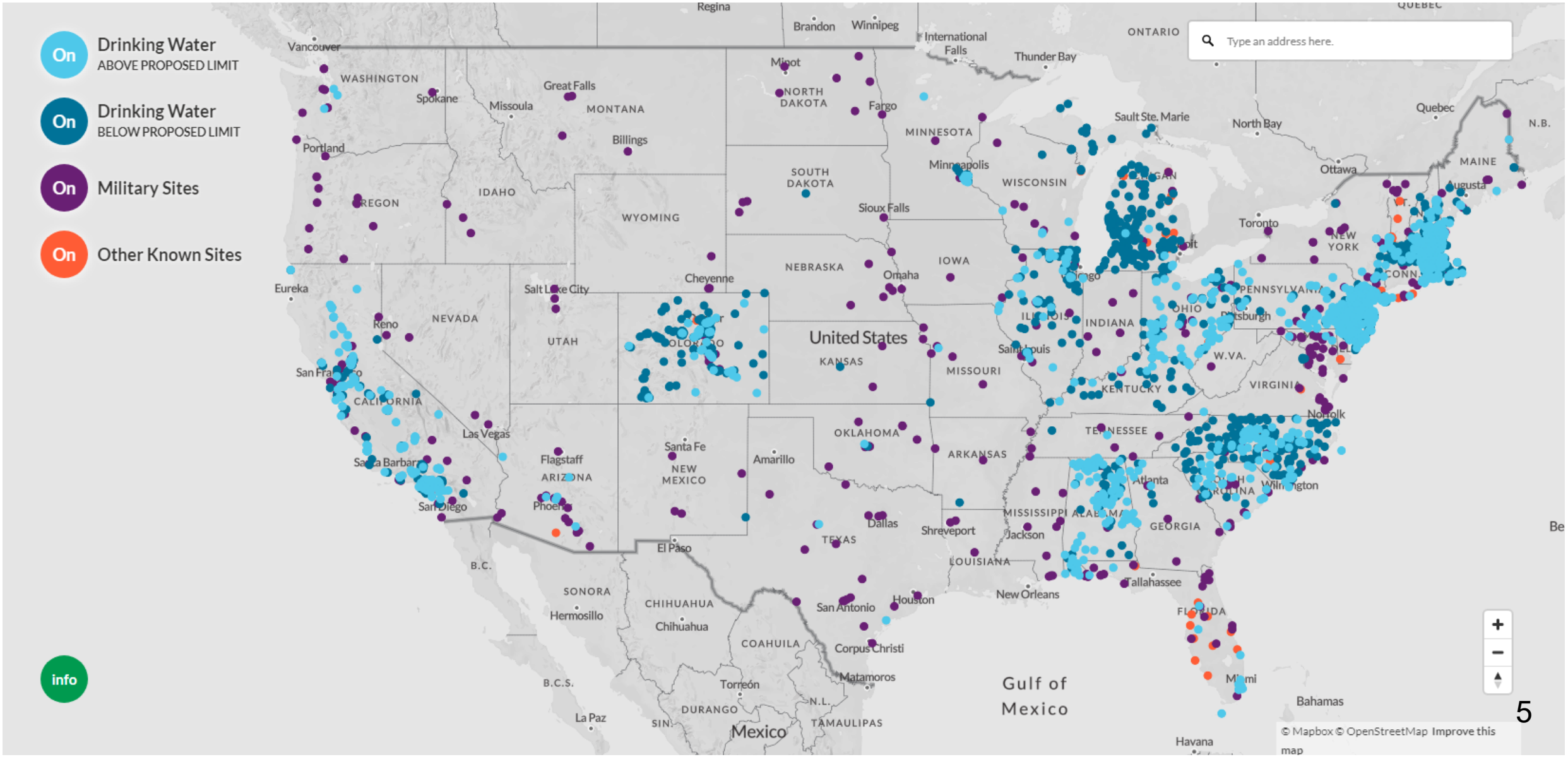

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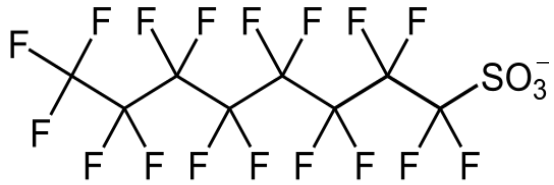
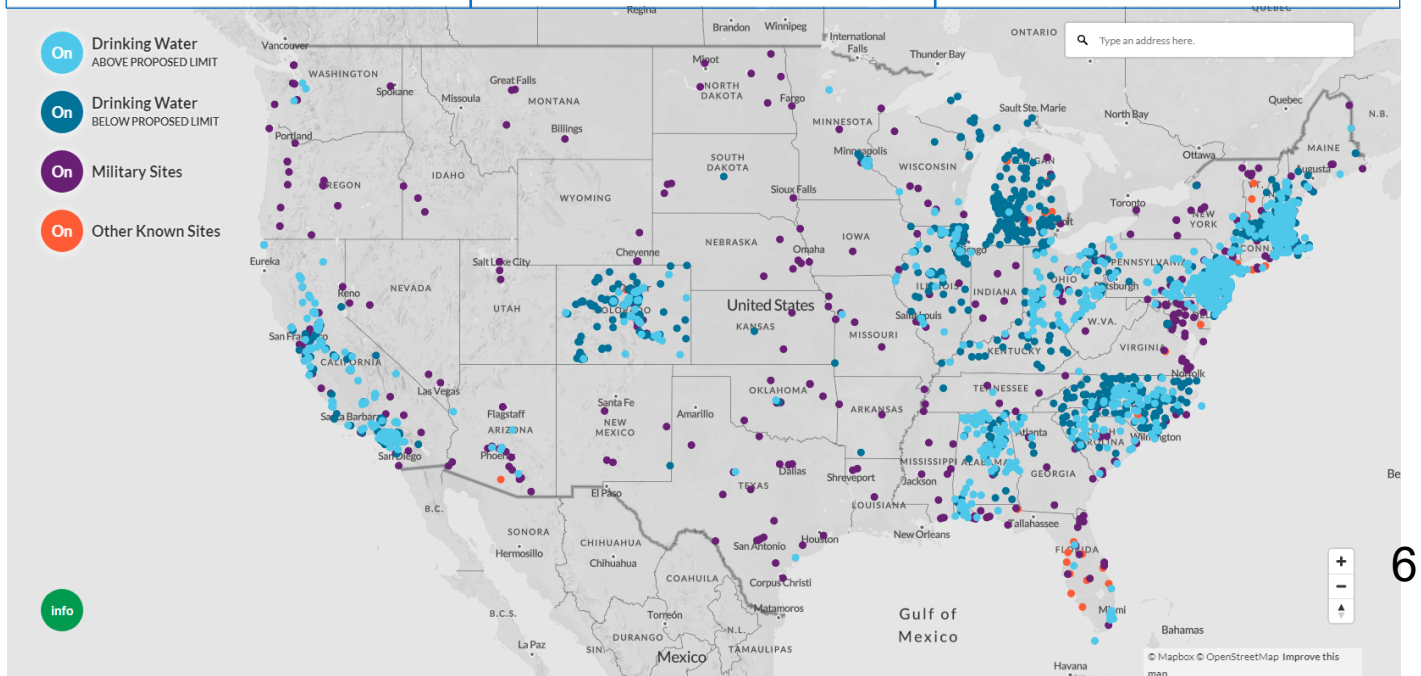


EPA's Proposed Action for the PFAS NPDWR

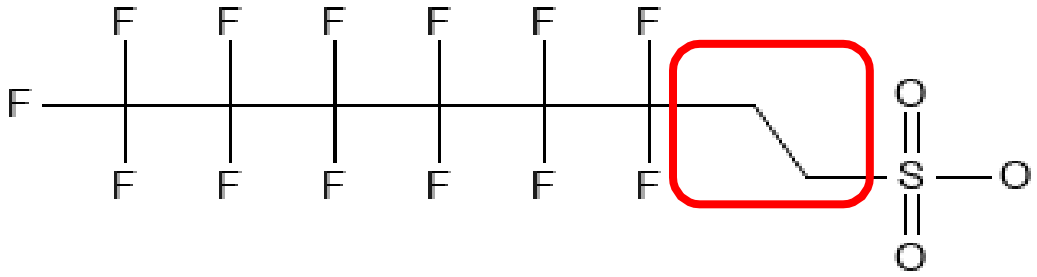
Compound	Proposed MCLG	Proposed MCL
PFOA	0 ppt	4 ppt
PFOS	0 ppt	4 ppt
PFNA	1.0 (unitless) Hazard Index	1.0 (unitless) Hazard Index
PFHxS		
PFBS		
HFPO-DA (GENX)		



PFAS categories

AFFF either Fluorotelomer (FT)-based or Electrochemical Fluorination-(ECF) based

FT= Partially fluorinated

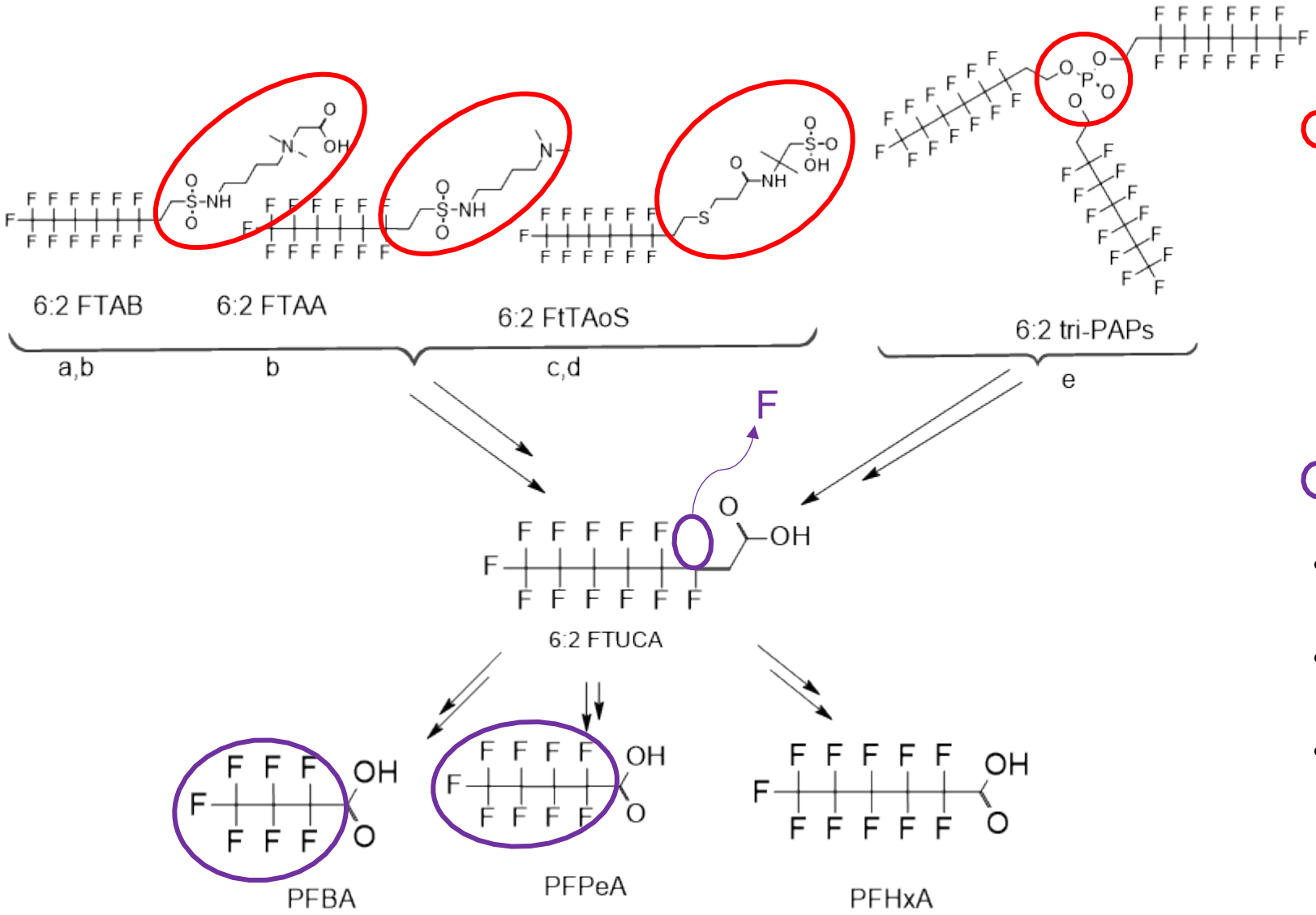


More reports of biotransformation including defluorination

ECF= Fully fluorinated

More recalcitrant, some reports of functional head group transformation

Types of PFAS transformation



Functional Group Transformations

- Occurs for both FT and ECF compounds

Fluorinated Tail Transformations

- Mainly observed with FT (exception: feammox)
- Progresses through a series of acids and ketones
- Complete bio-defluorination yet to be shown

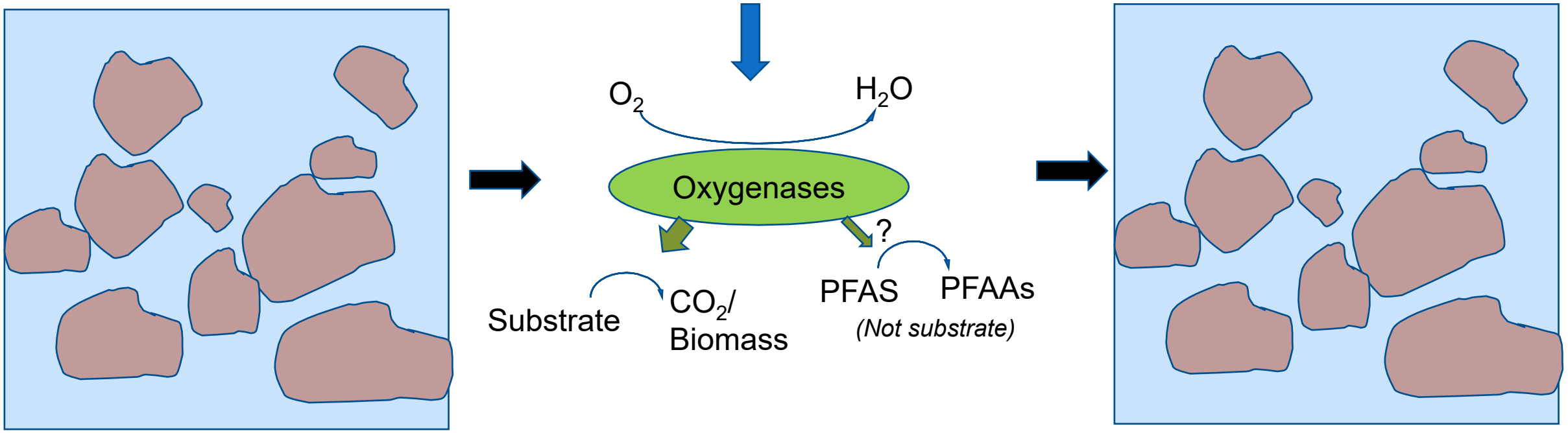
LaFond, J. et al., 2023, under revision

Potential application of biotransformation in aquifers

Large functional groups ~ harder to remove from soils

Oxygenases known to catalyze co-metabolic reactions in contaminated soils

Smaller anionic functional groups ~ easier to remove



Research Question:

Can oxygenases catalyze conversion of precursors to PFAAs?

Persulfate oxidation: Shojaei et al 2021: DOI: 10.1021/acs.est.0c08069

Groundwater studies: set up

Live Treatments

- Methanotroph consortium
- Isobutane oxidizer consortium
- Pentane oxidizer consortium
- Octane oxidizer consortium
- *Rhodococcus ruber* (Propane)
- *G4 Pseudomonas cepacia* (Toluene)

Suspect Screening + Non-target

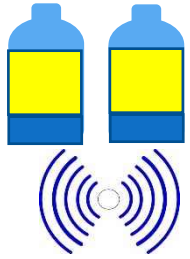
Targeted Analysis

Headspace measured weekly, GC

Site-impacted groundwater

Orbital shaker

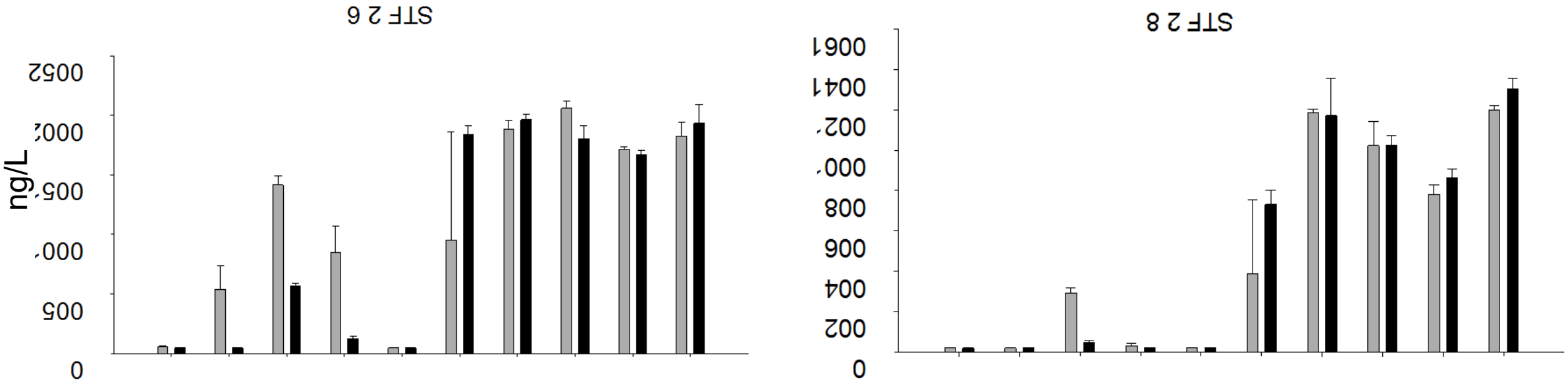
4 & 8 weeks

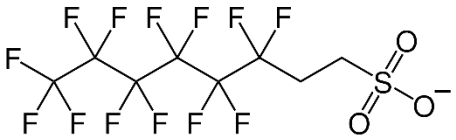


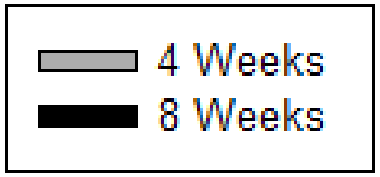
X2 MeOH
2hr heated sonication

Site Screening Study: Fluorotelomer (FT) Results

FTS transformation by oxygenases

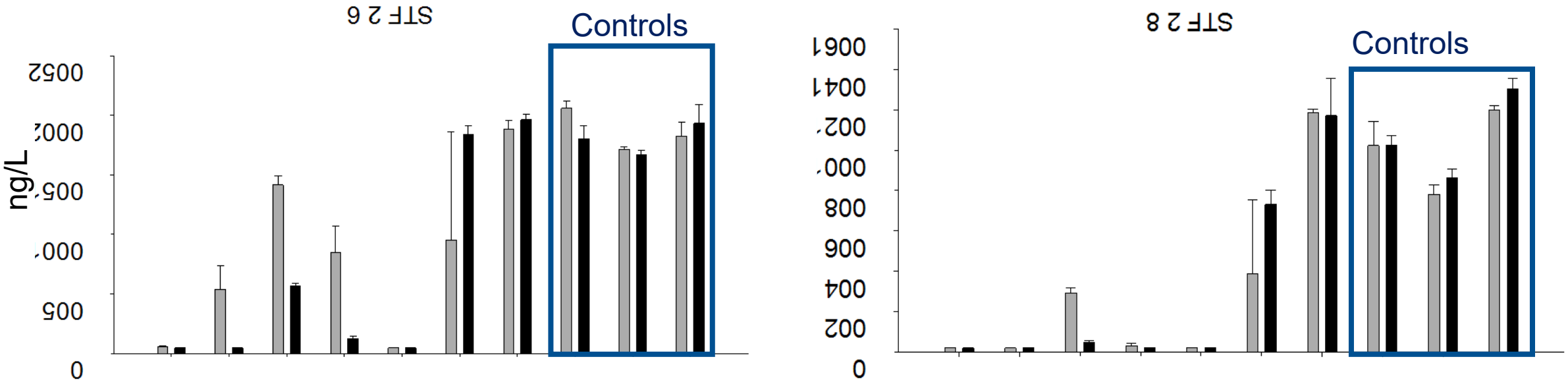






LaFond, J. et al., 2023, in preparation

FTS transformation by oxygenases



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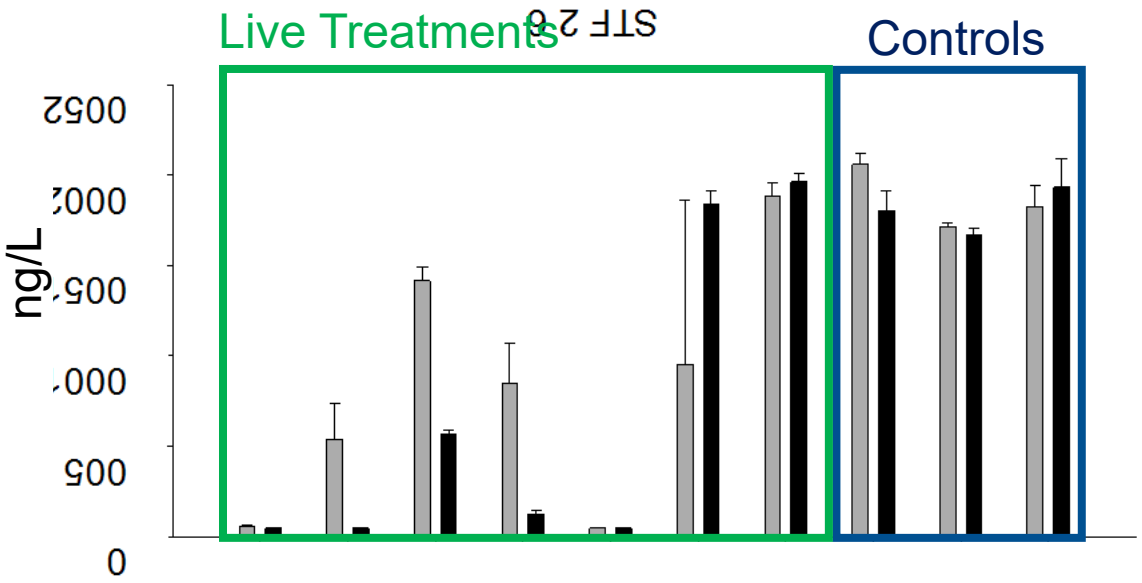

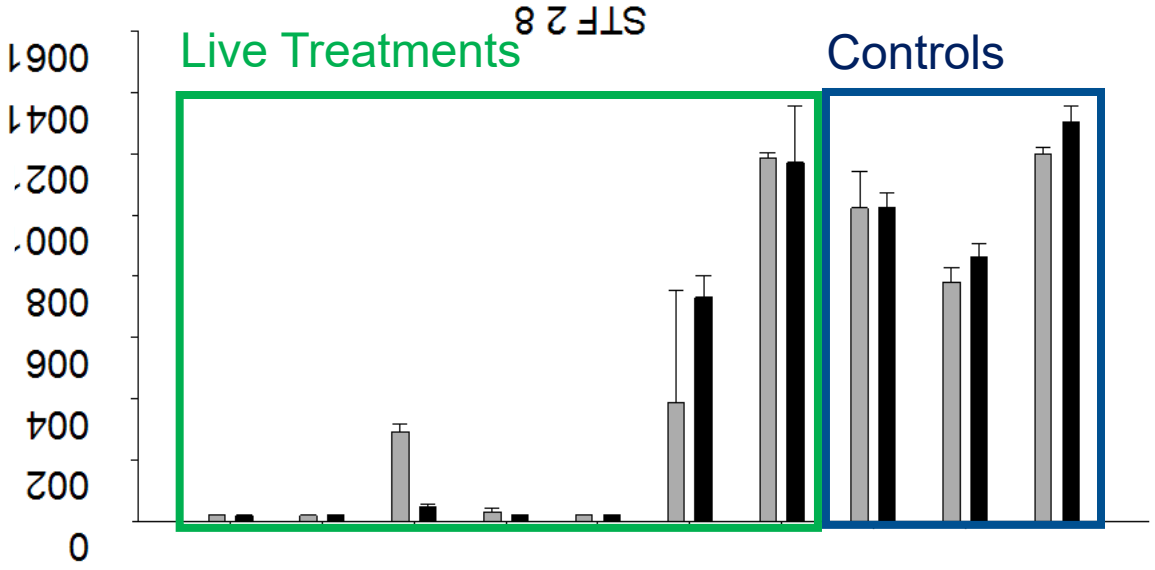

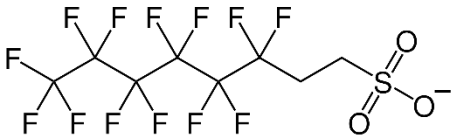

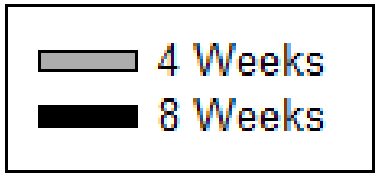

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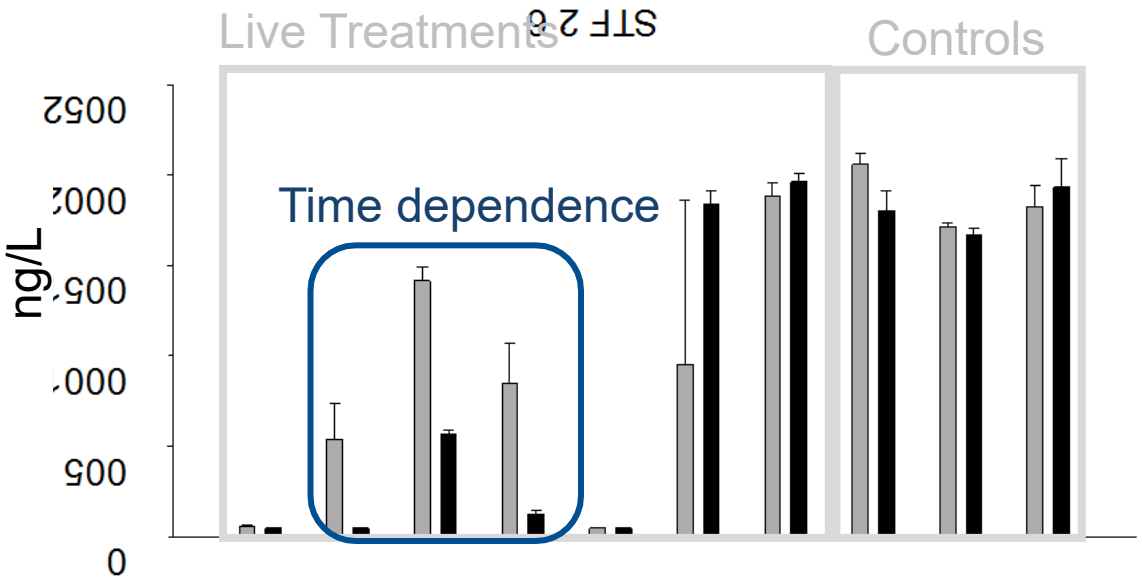

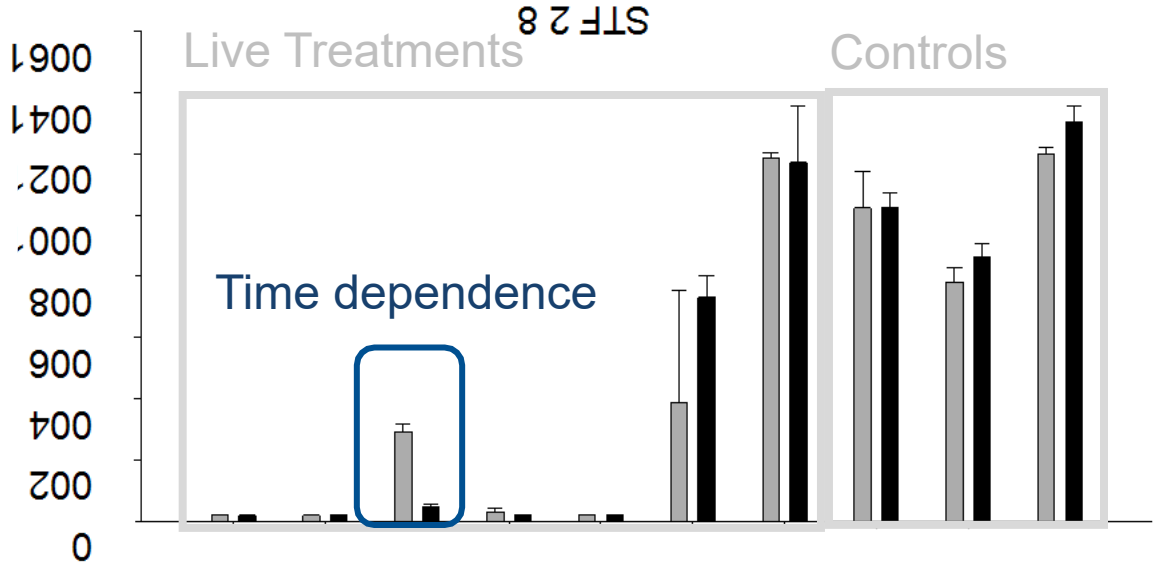

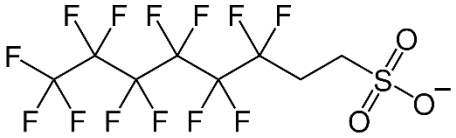

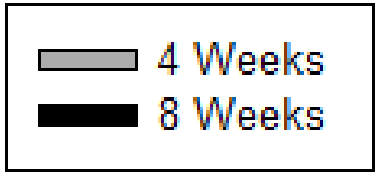

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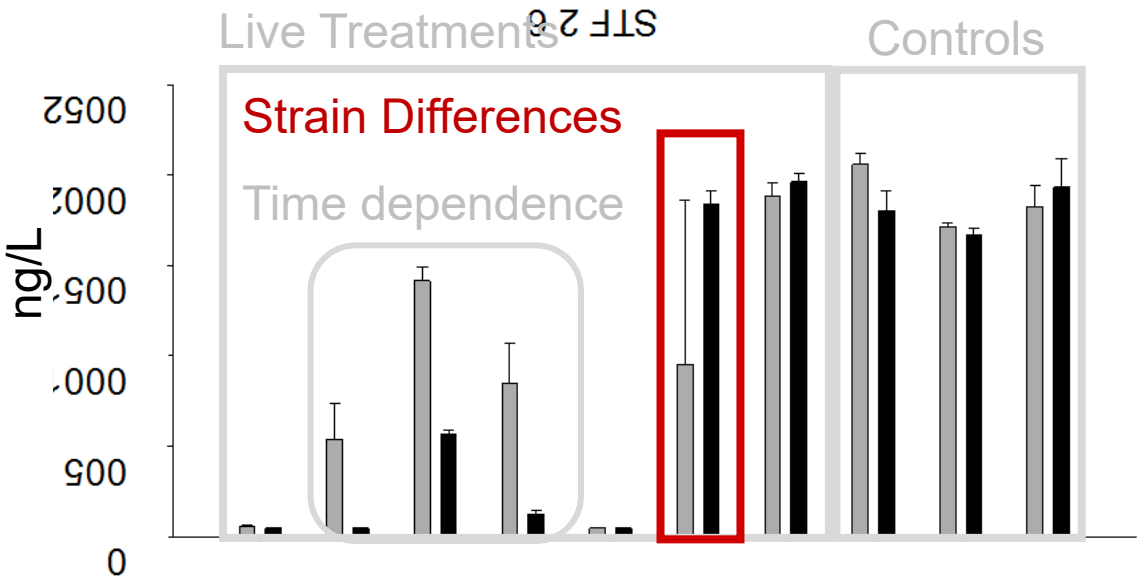

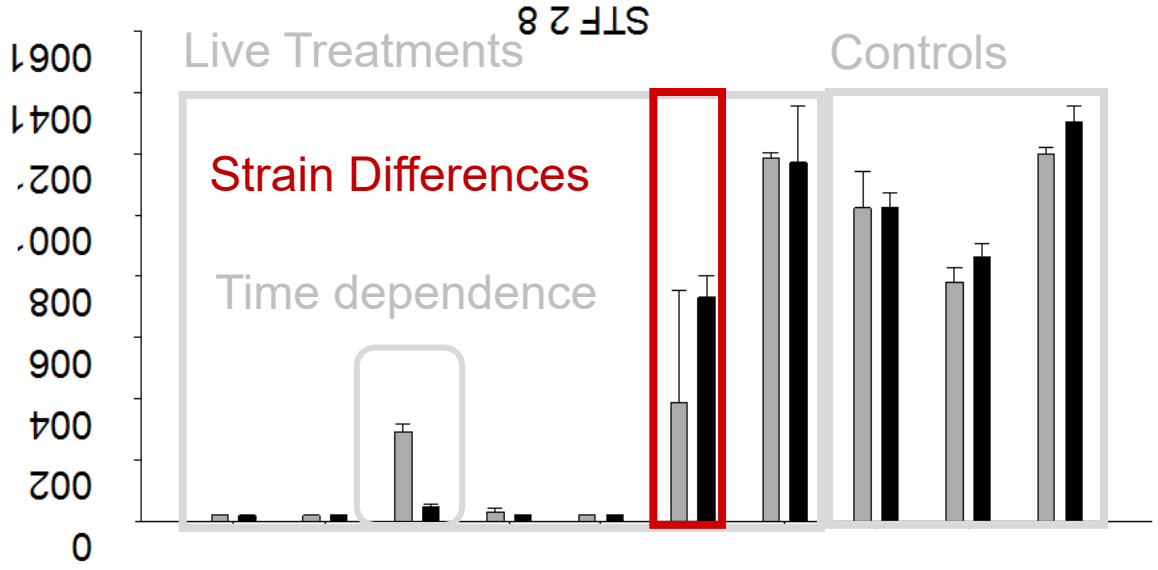

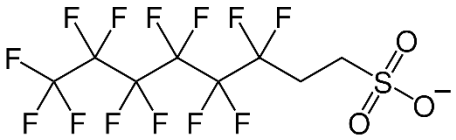

4 Weeks
8 Weeks

16

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6:2 FTS Pure compound study set up

Live Treatments

- Methanotroph consortium
- Octane oxidizer consortium
- *Methylocystis hirsuta* (Methane)
- *Rhodococcus ruber* (Propane)
- *G4 Pseudomonas cepacia* (Toluene)

Suspect Screening + Non-target

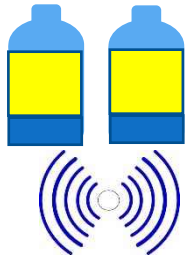
Targeted Analysis

Headspace measured weekly, GC

6:2 FTS

Orbital shaker

4 & 8 weeks



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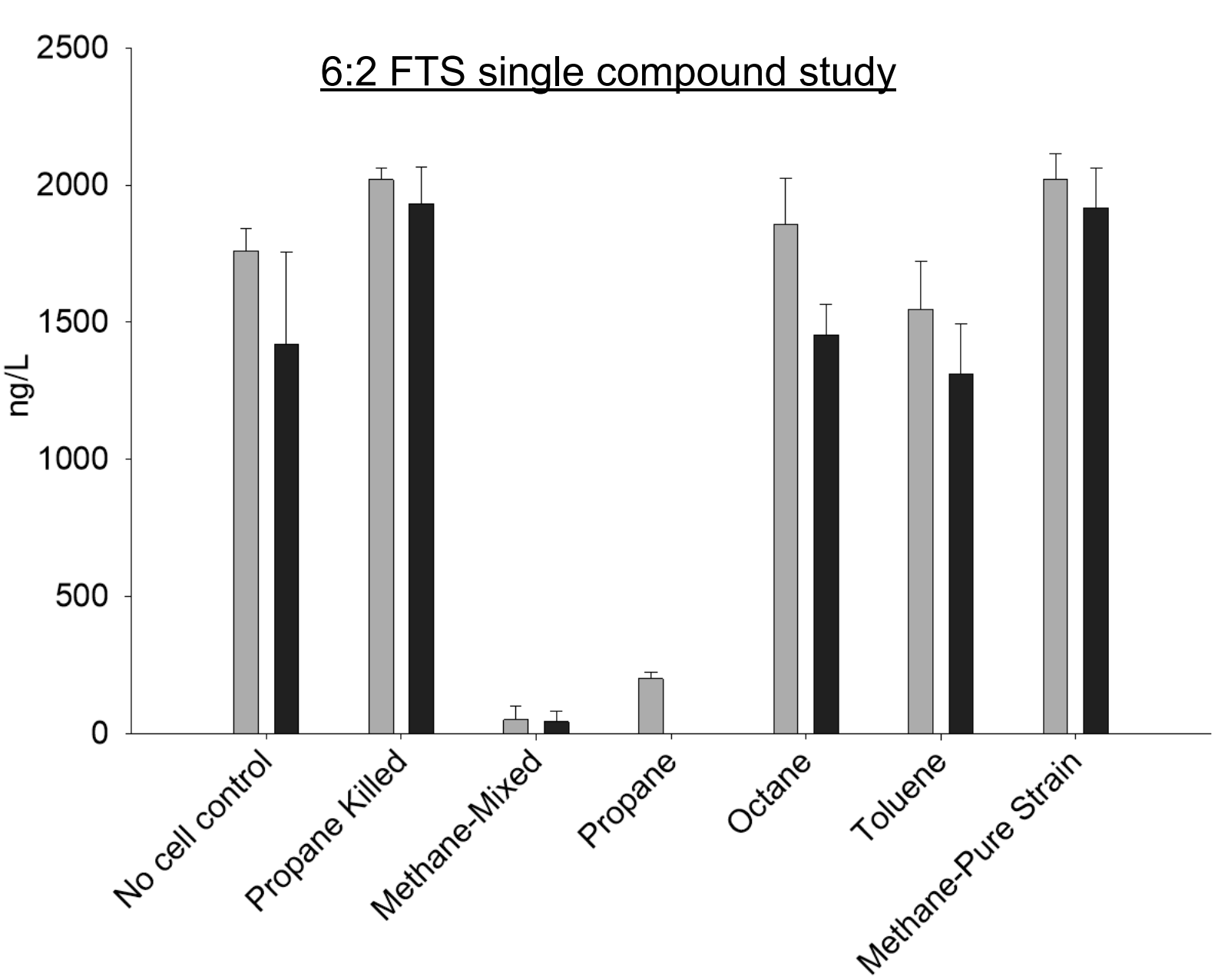
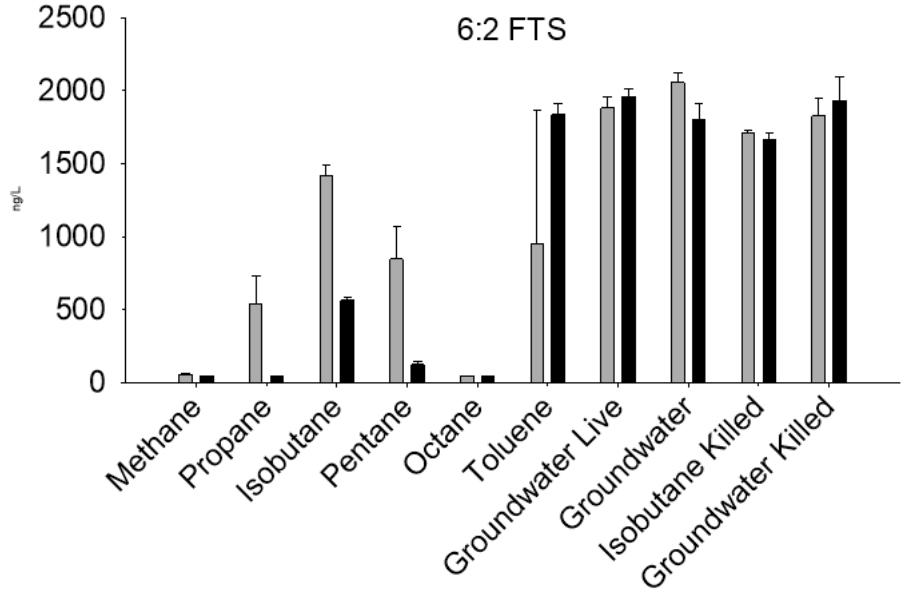
Replication of 6:2 FTS transformation

6:2 FTS single compound study



Groundwater study (shown previously)



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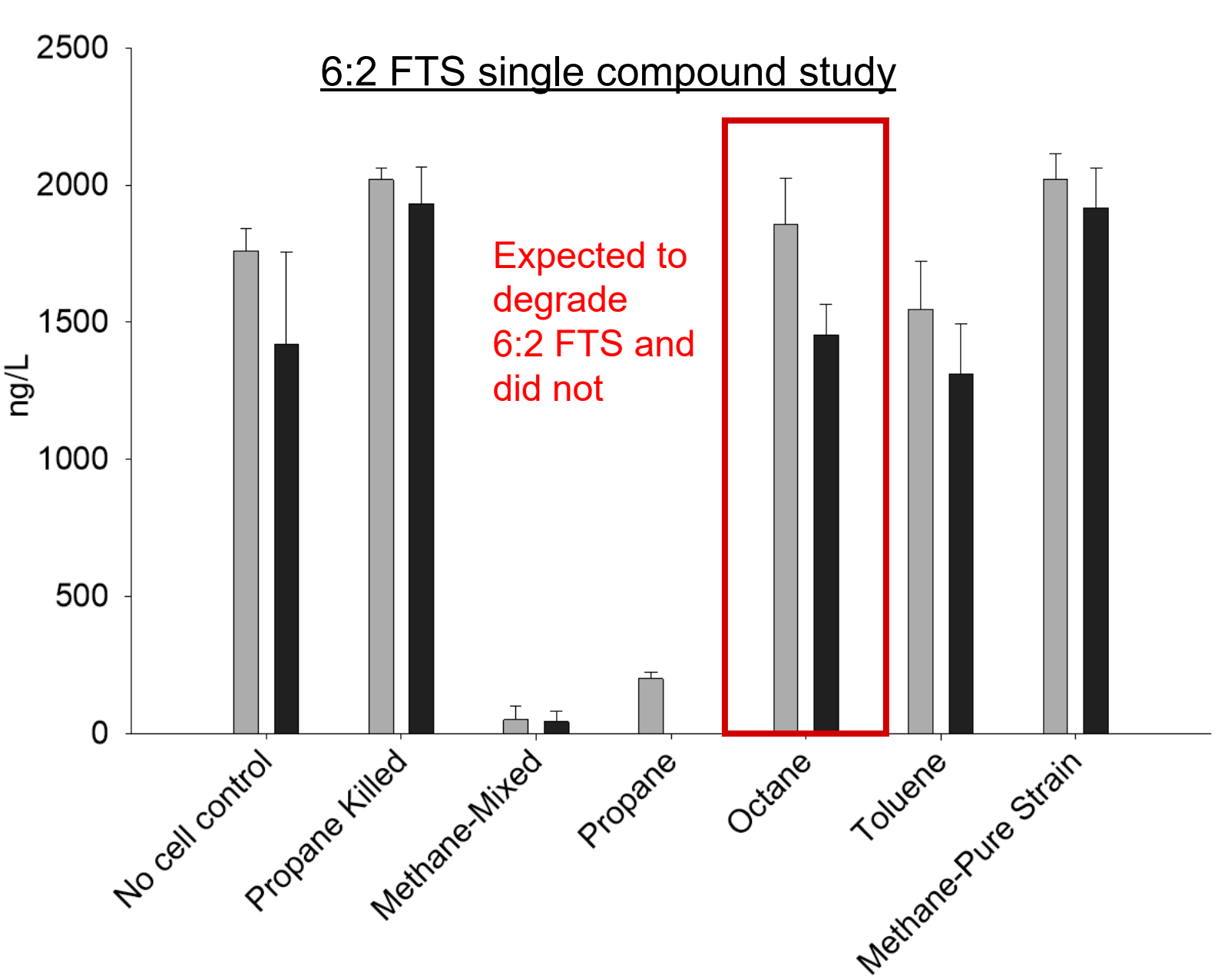

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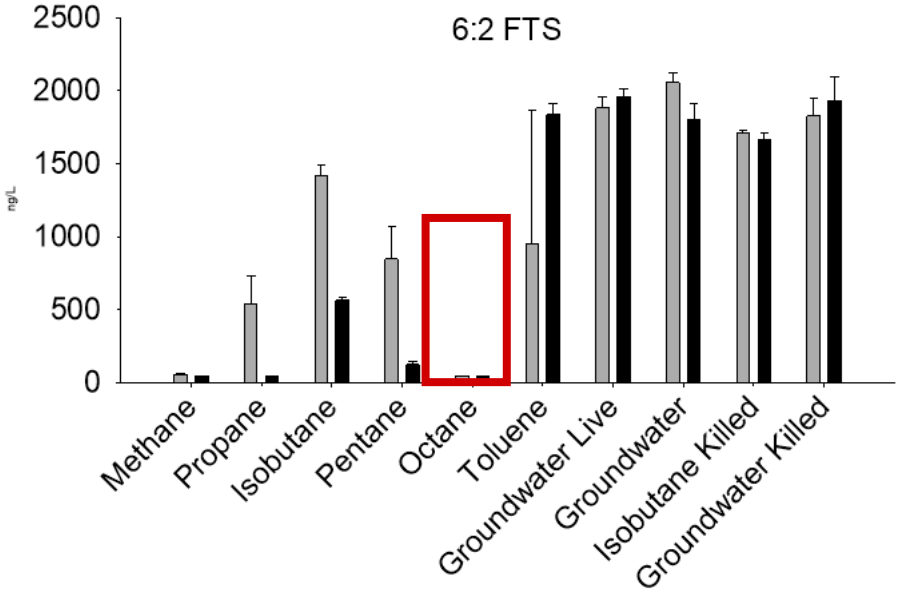

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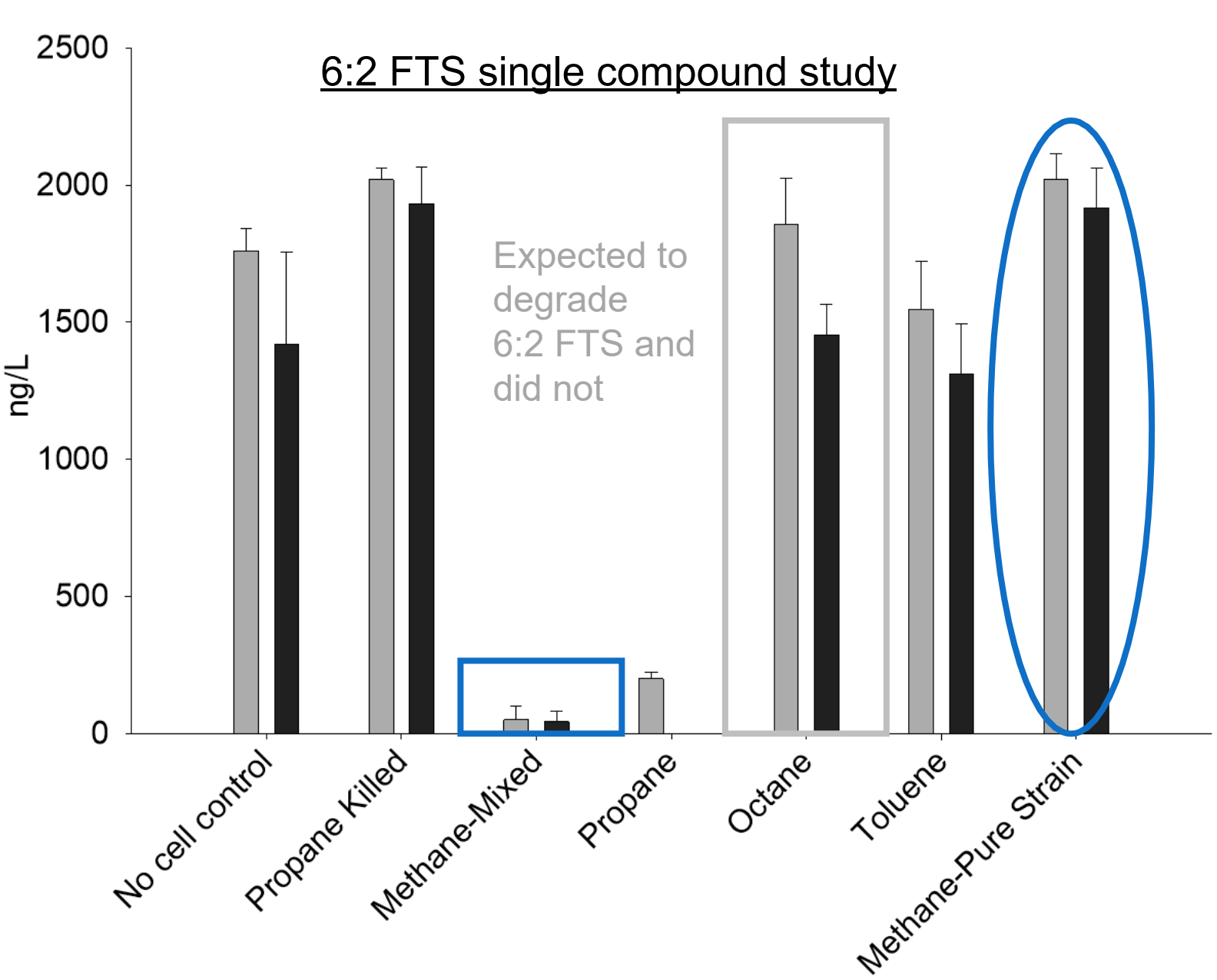

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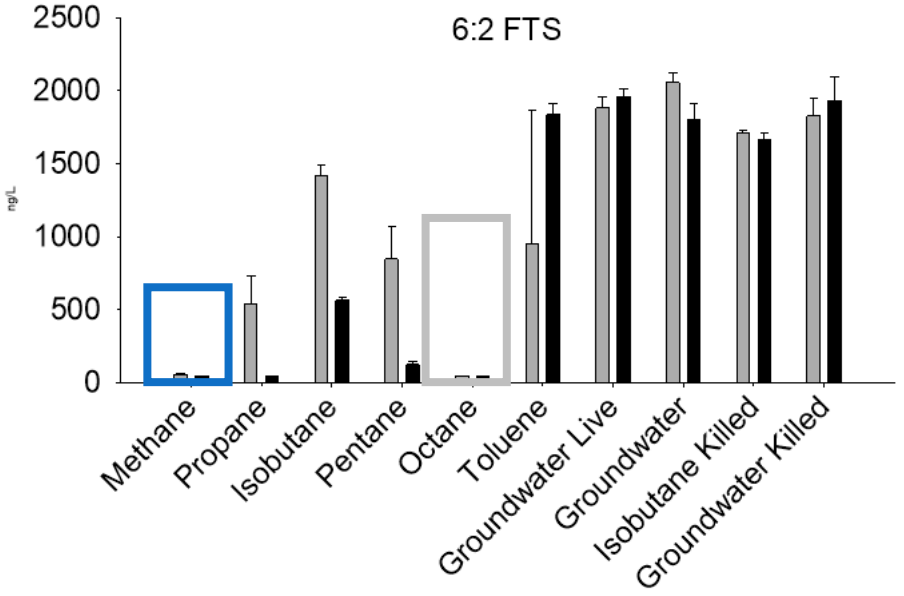

Possible that not every methanotroph can catalyze transformation

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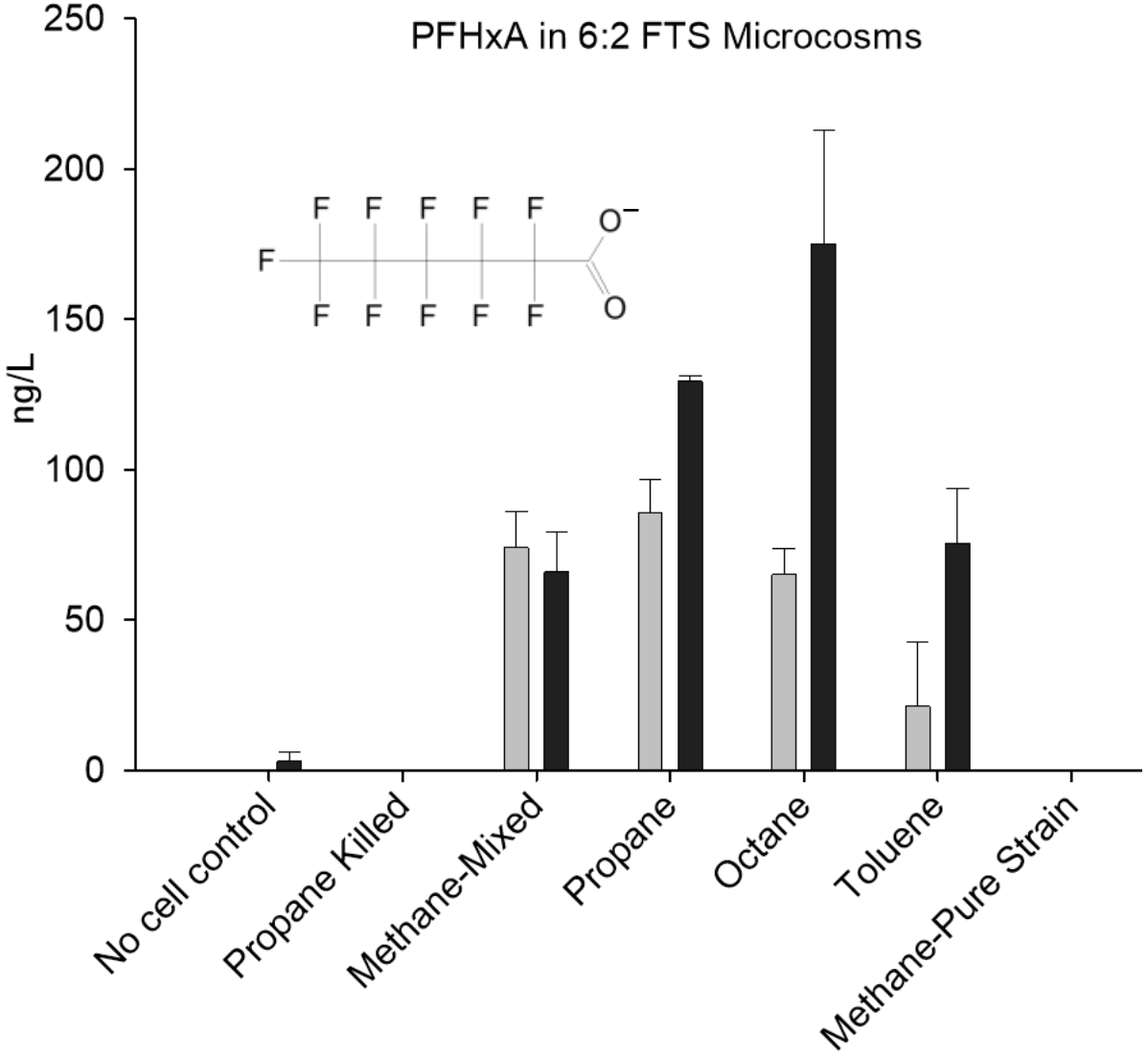
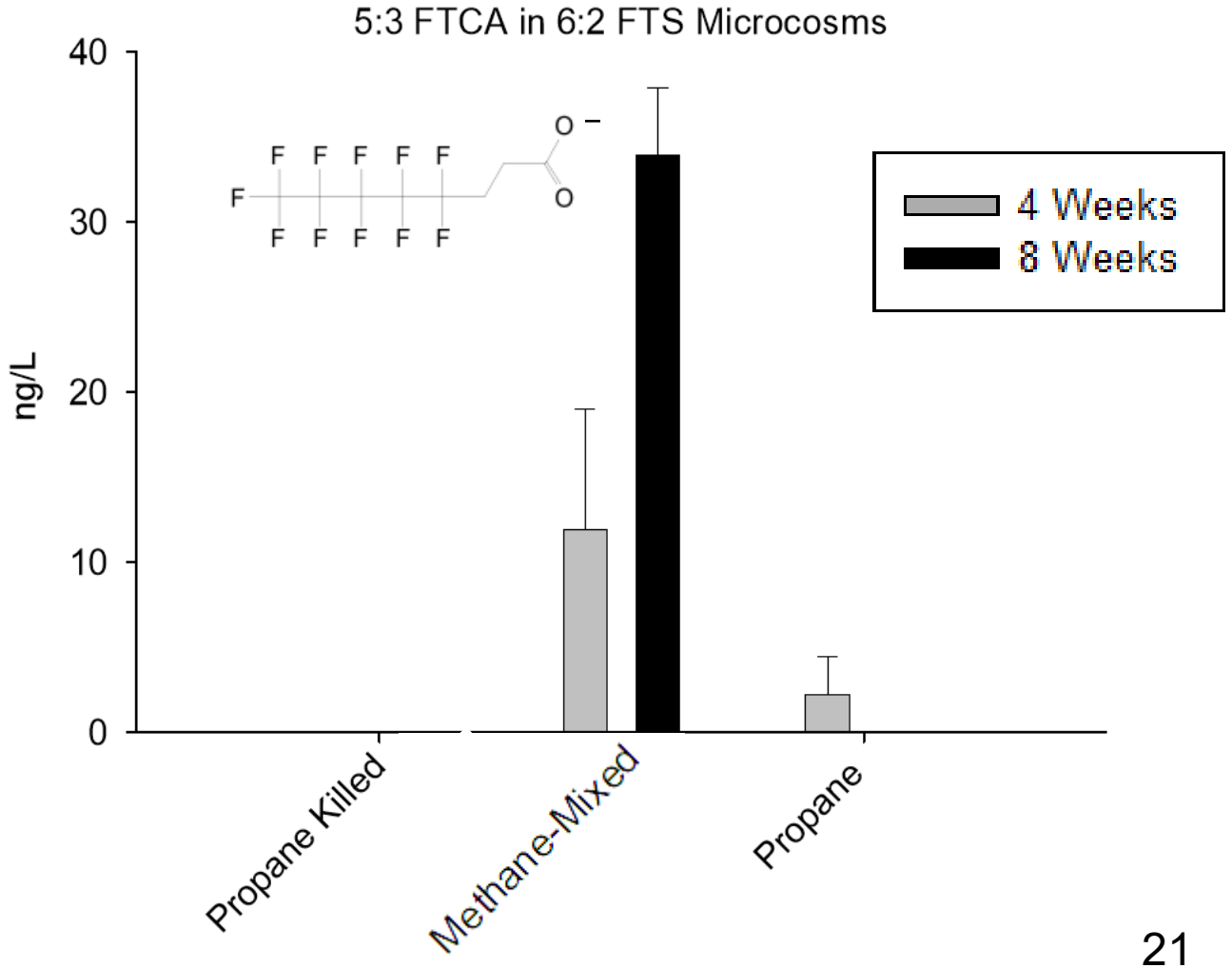
6:2 FTS Terminal products

- So where did the 6:2 FTS go in the Propane and Mixed Methane treatments?





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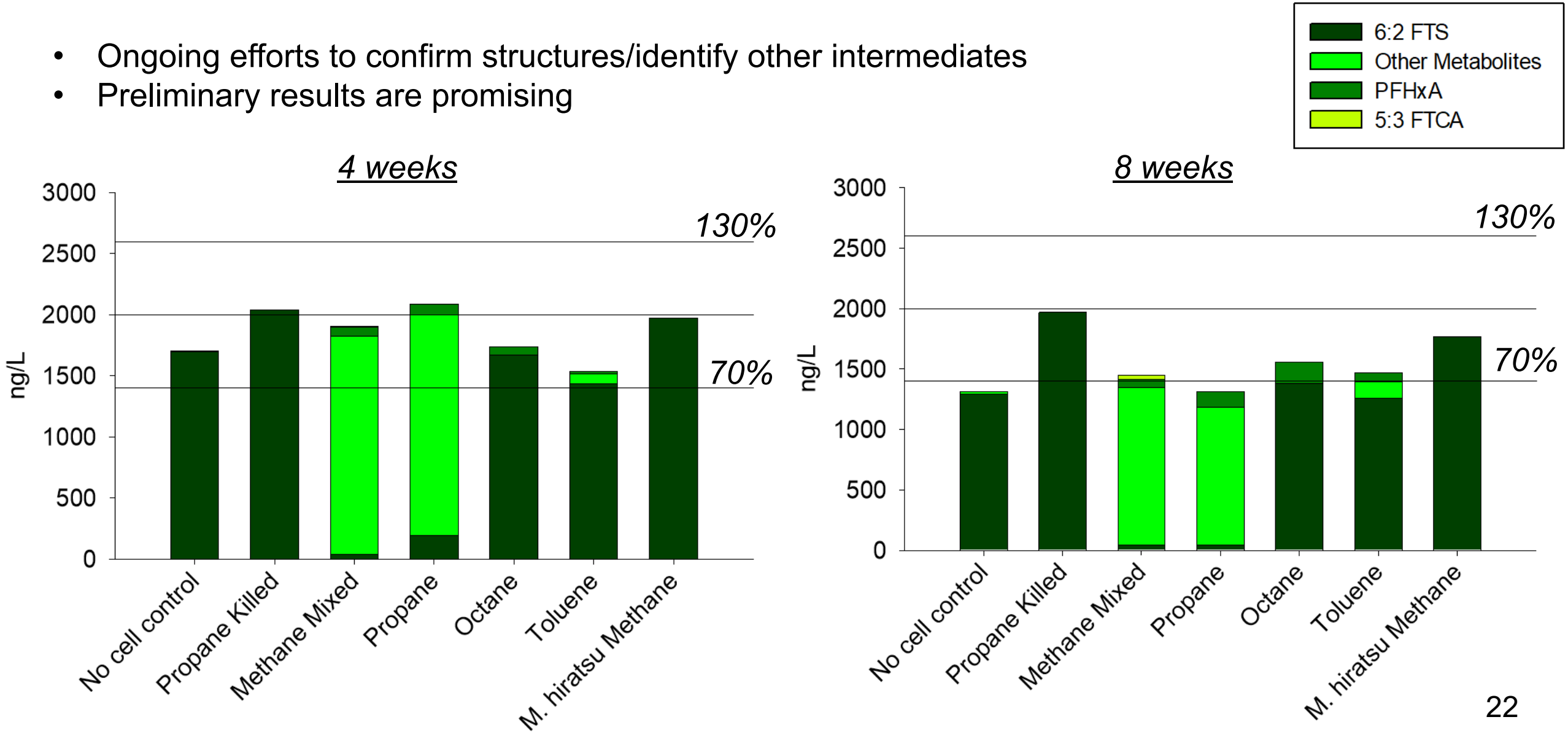
Closing the mass-balance with non-target analysis

- Ongoing efforts to confirm structures/identify other intermediates
- Preliminary results are promising



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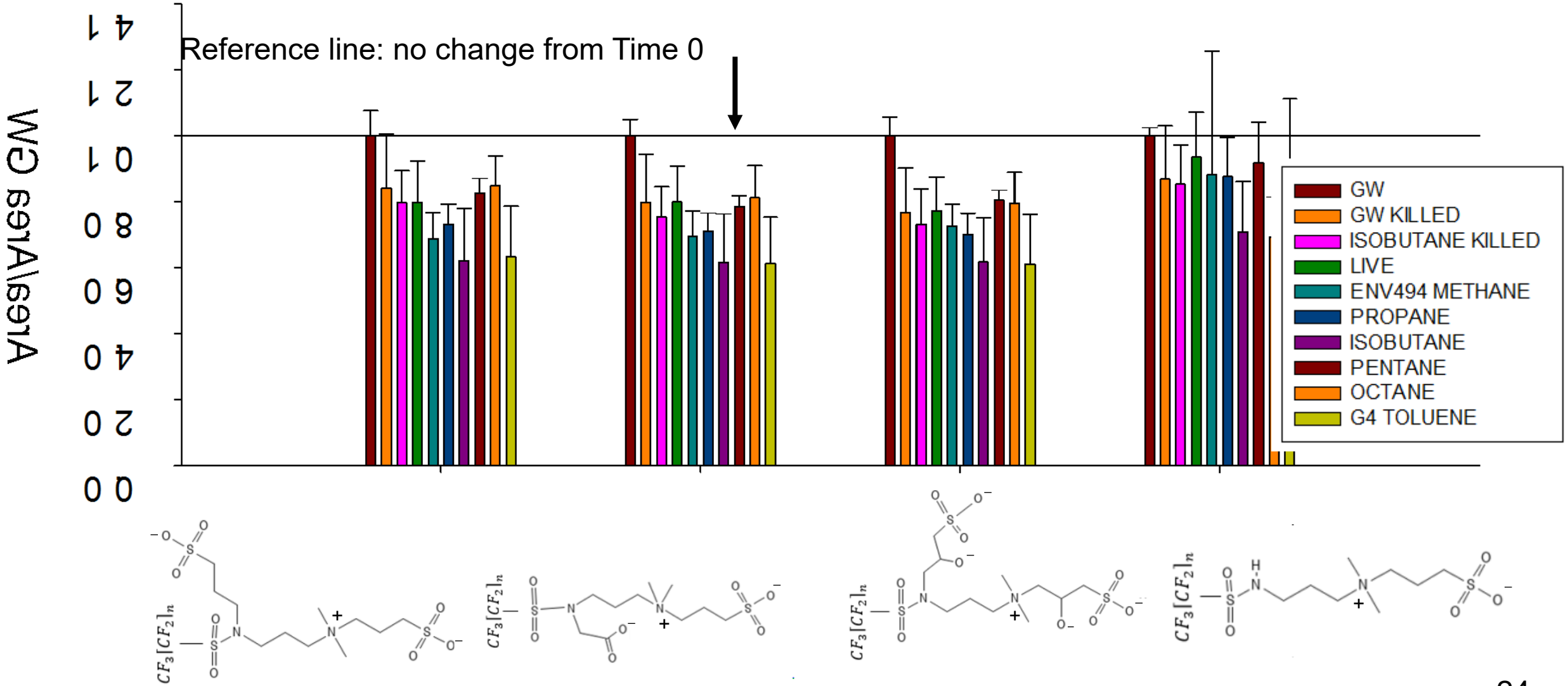
Site Screening Study: ECF Results

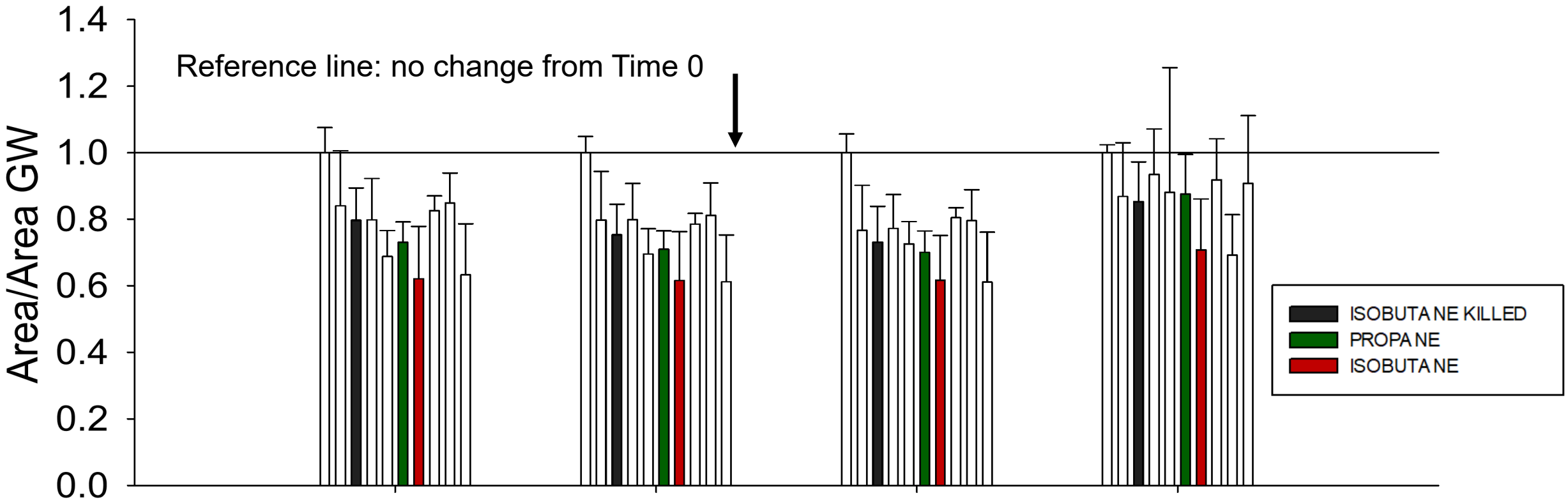
Decreases in PFAA-precursors at 4 weeks

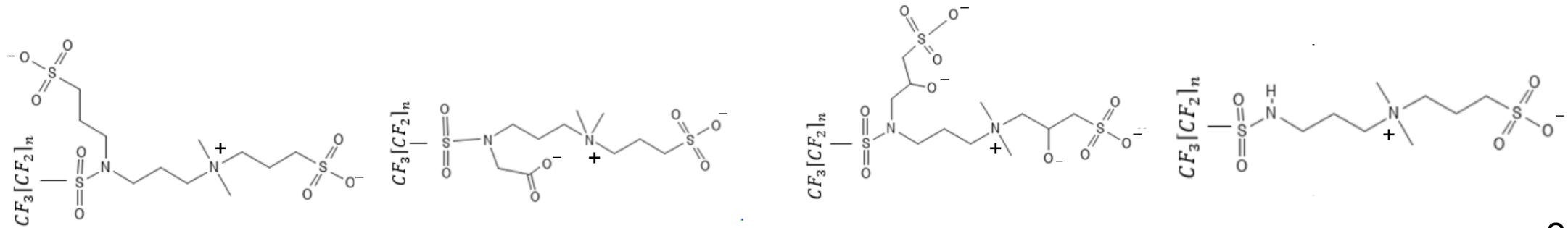


SPrAmPr-FHxSAPrS SPrAmPr-FHxSAA S-OHPrAmPr-FHxSA-OHPrS S-OHPrAmPr-FHxSA

LaFond, J. et al., 2023, in preparation

Decreases in PFAA-precursors at 4 weeks Isobutane + Propane cultures





SPrAmPr-FHxSAPrS SPrAmPr-FHxSAA S-OHPrAmPr-FHxSA-OHPrS S-OHPrAmPr-FHxSA

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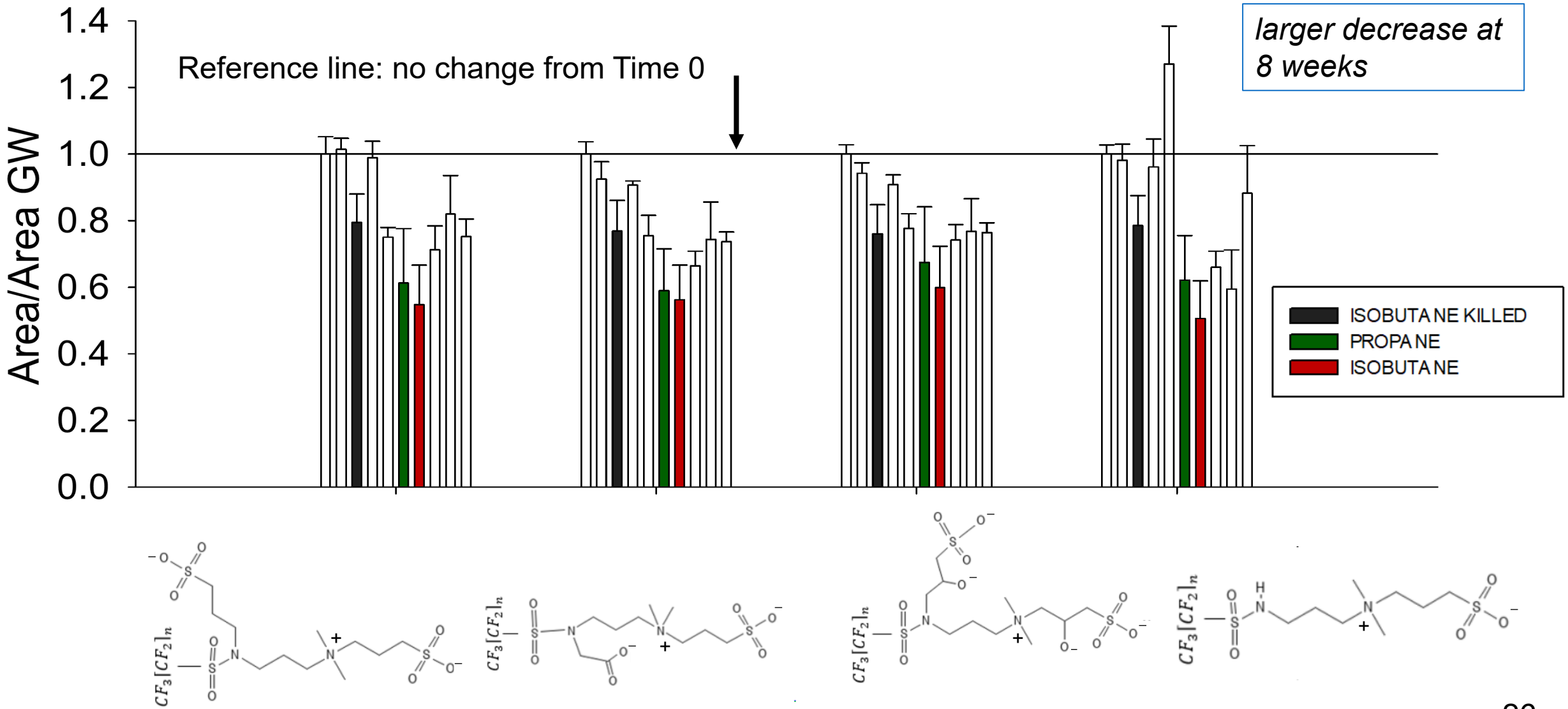
Decreases in PFAA-precursors at 8 weeks Isobutane + Propane cultures



SPrAmPr-FHxSAPrS SPrAmPr-FHxSAA S-OHPrAmPr-FHxSA-OHPrS S-OHPrAmPr-FHxSA

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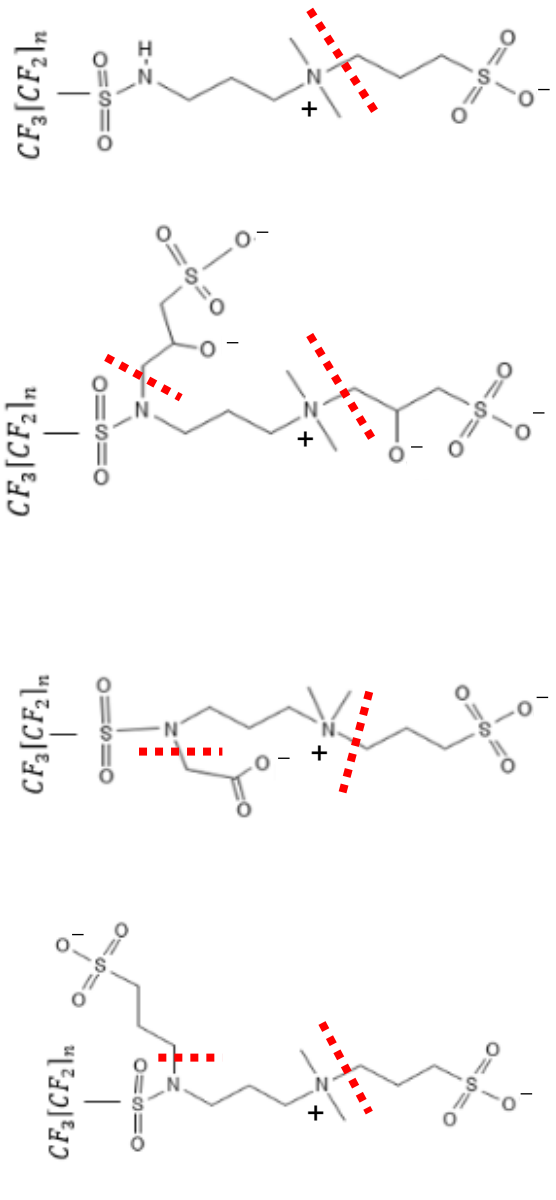
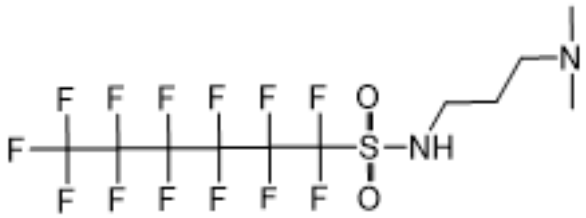
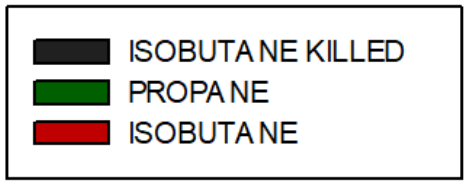
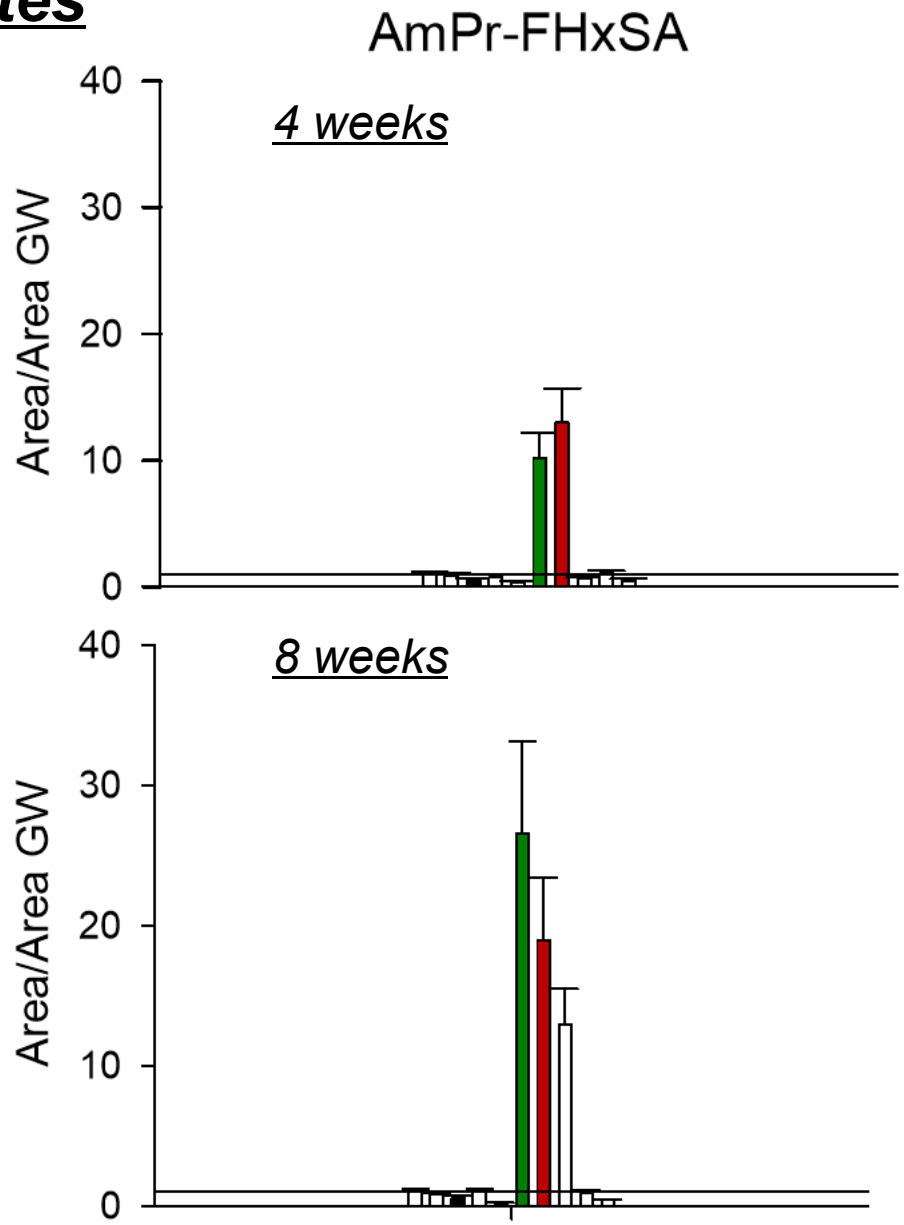
Potential intermediates









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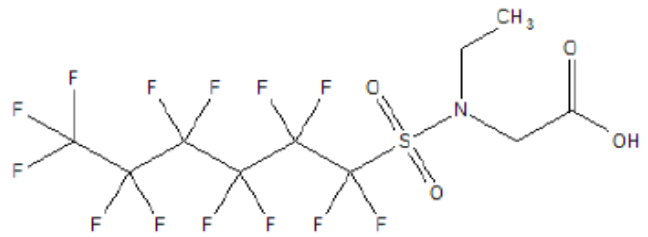
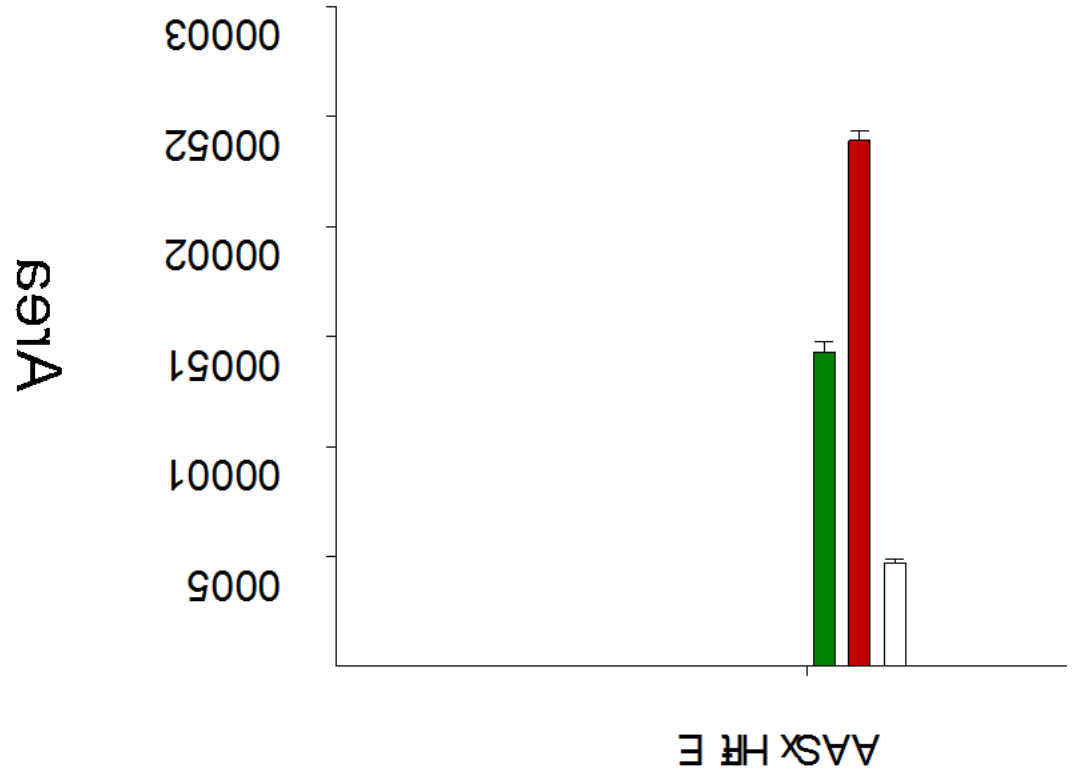
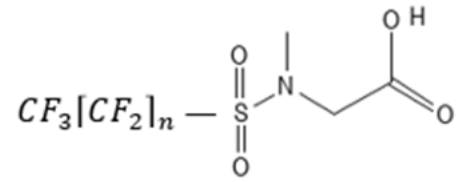
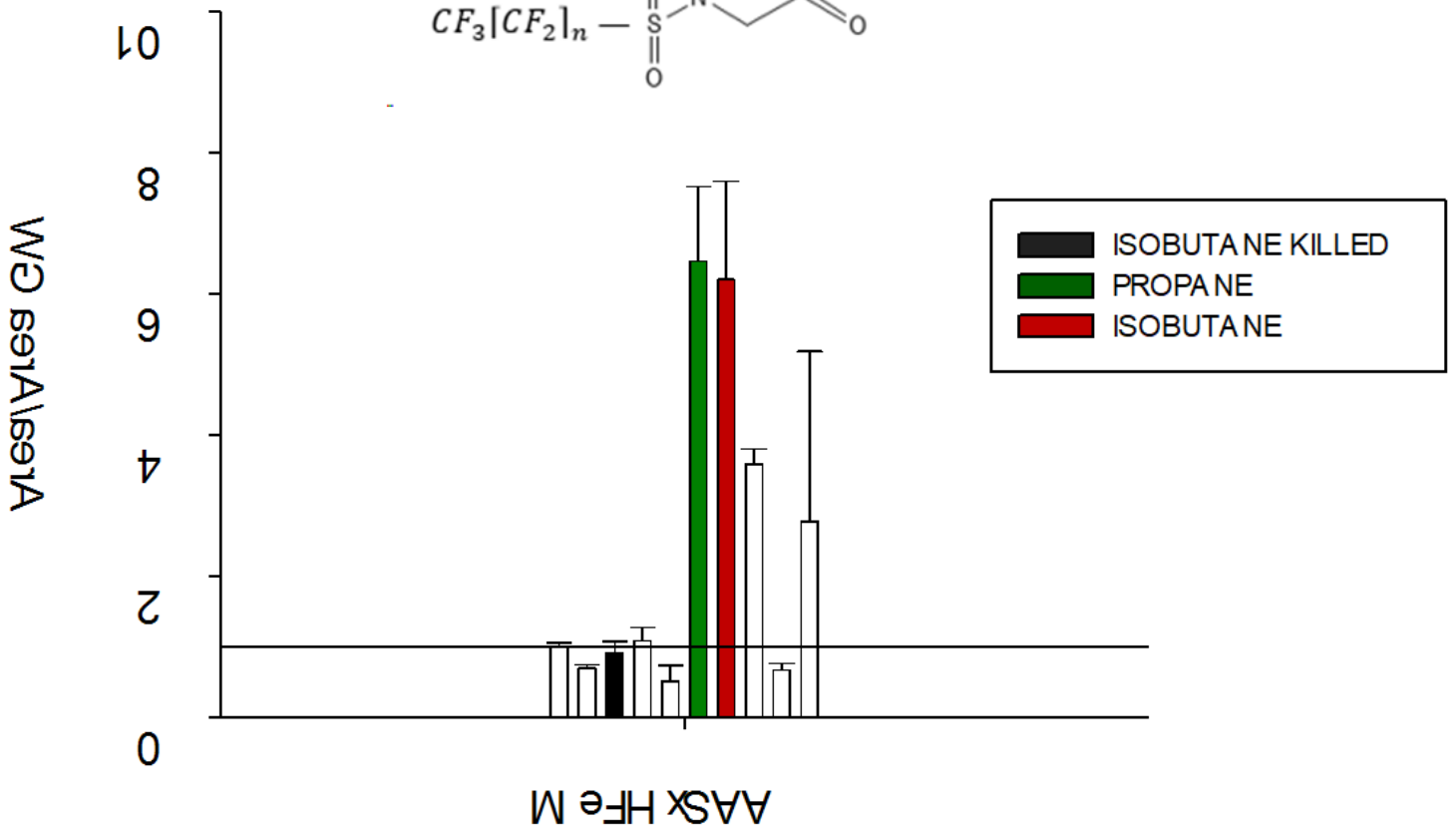
Smaller intermediates observed (8wks)









*only present in propane, isobutane, pentane

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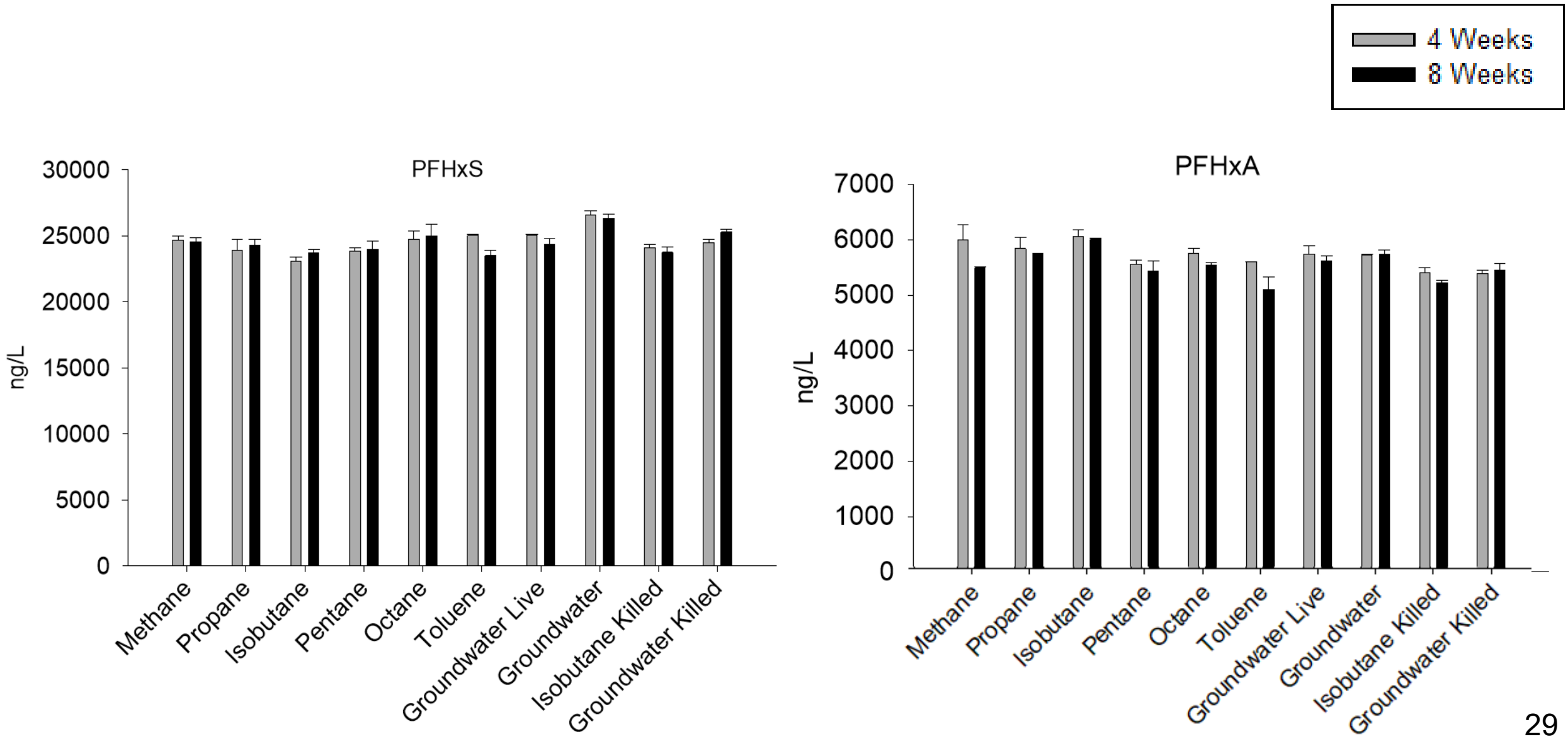
Is there an increase in terminal PFAAs?



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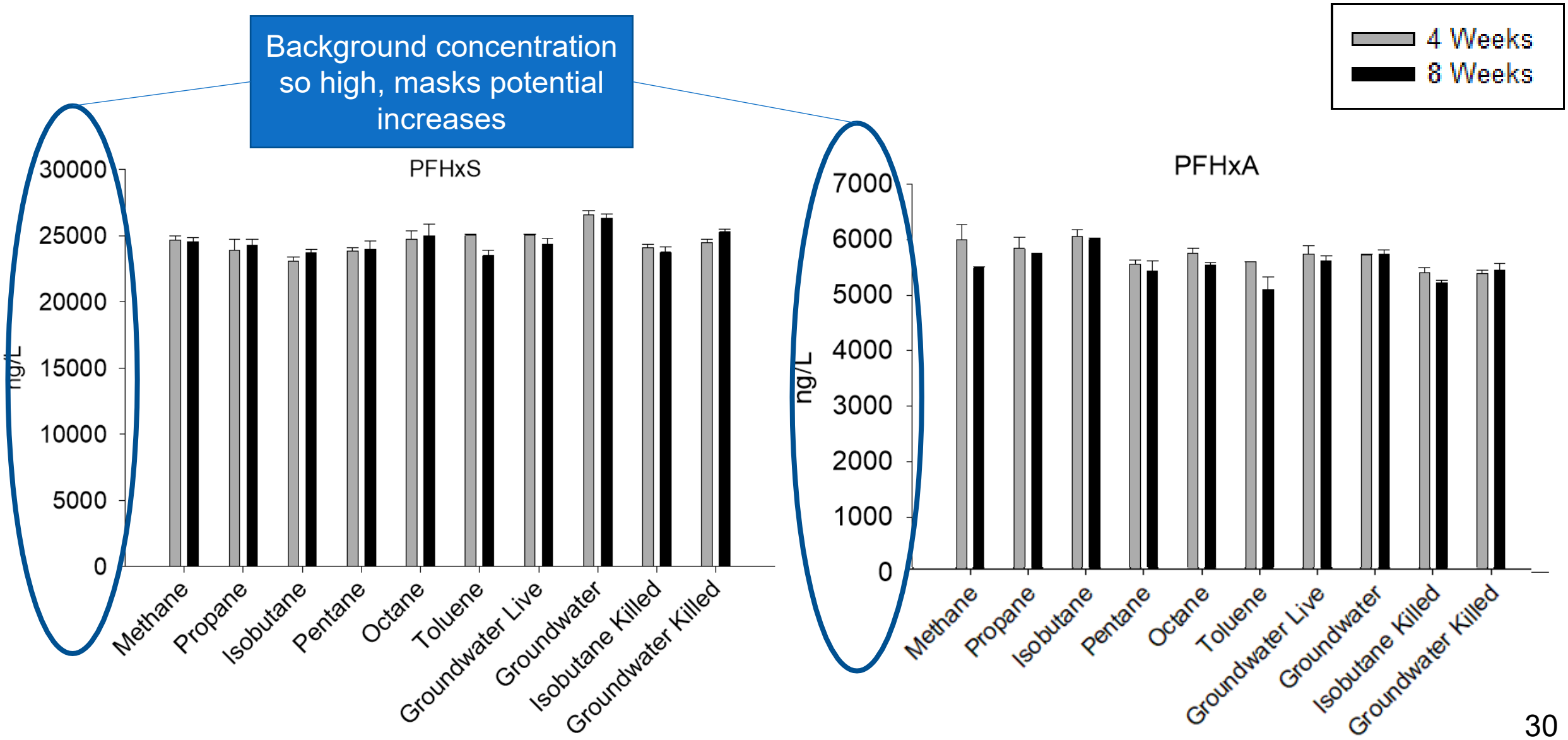
Is there an increase in terminal PFAAs?

Background concentration so high, masks potential increases



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Main take aways

- Observed a decrease in 6:2 and 8:2 FTS in consortia grown on propane, methane, octane, isobutane, and pentane. Not with toluene
- Confirmed 6:2 FTS transformation in pure-compound studies with propane and methane
- Did not replicate results with octane nor saw transformation with pure strain of methanotrophs
- Observed transformation of ECF functional groups in propane and isobutane

Substrate	Type	Transformation? FT	ECF
Methane	Pure Strain	✗	n.d.
Methane	Consortia	✓	✓
Propane	Pure Strain	✓	✓
Isobutane	Consortia	✓	✓
Pentane	Consortia	✓	✓
Octane	Consortia	✓/?	✓
Toluene	Pure Strain	✗/?	✓

Next steps and potential applications

Next Steps:

- ECF pure compound studies
- Stimulating native organisms by adding different substrates
  - i.e. methane/octane etc.
  - Using different sites to confirm widespread applicability

How is this useful?

Hopefully identify organisms that can be stimulated to catalyze conversion of precursors to PFAAs for sites where PFAS flushing is desired.

Acknowledgements

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Key Points

- Both FT and ECF based precursors showed conversion of the functional headgroup
- FT based precursors showed shortening of the fluorinated tail
- Transformation varied by compound and organism

Thank you!

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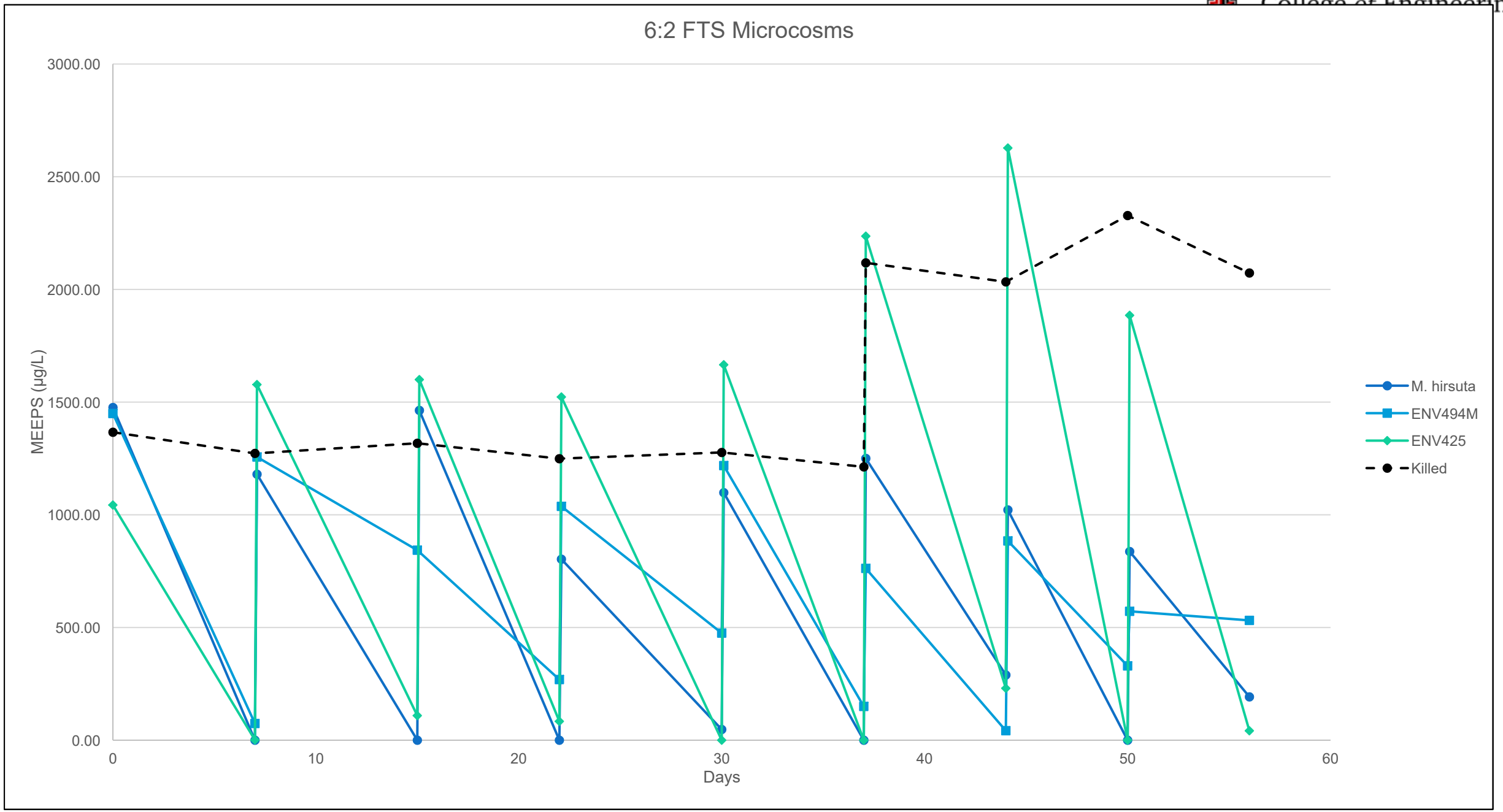
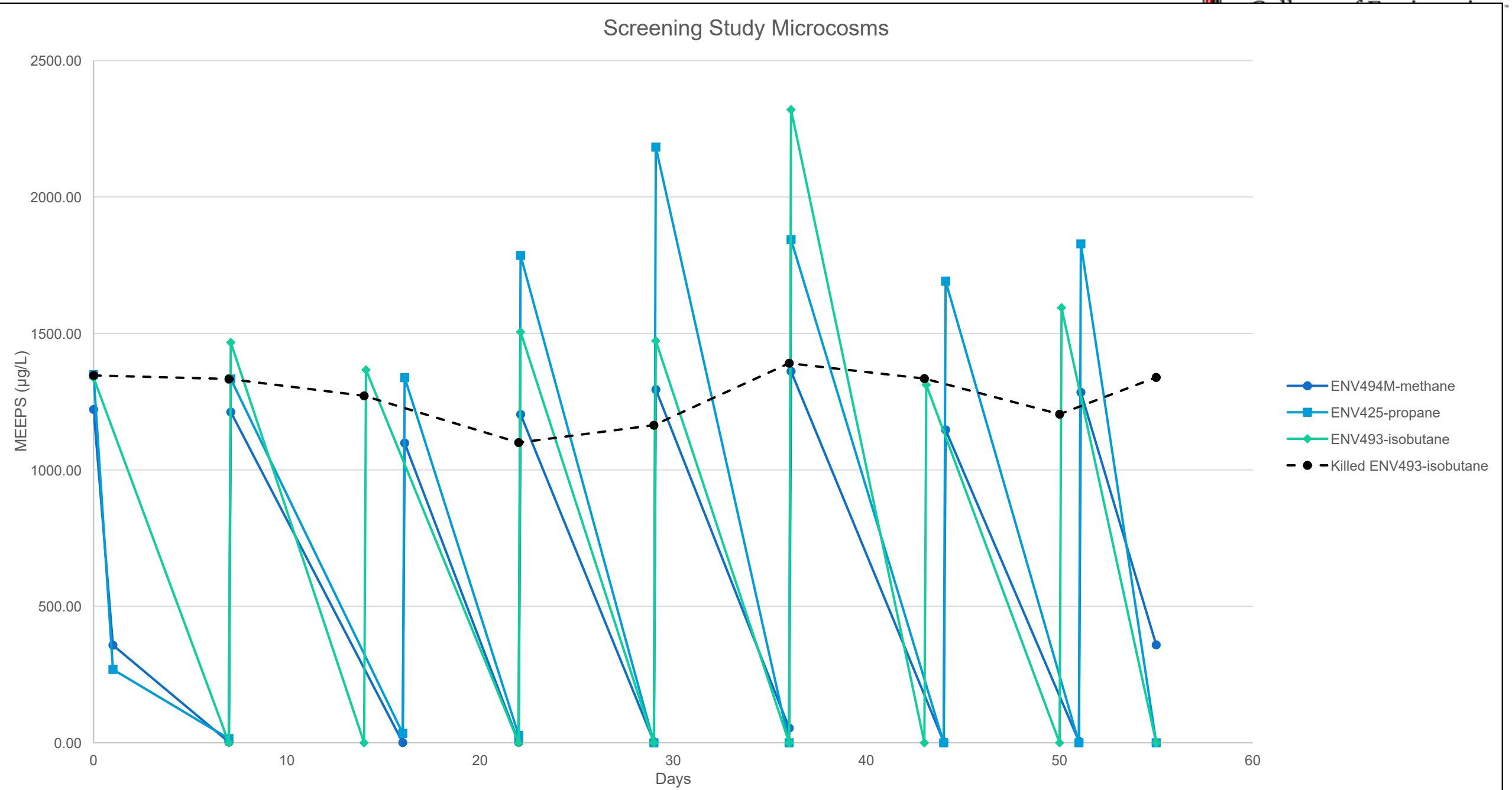
Backup Slides


6:2 FTS Microcosms
3000.00
2500.00
2000.00
1500.00
1000.00
500.00
0.00
MEEPS (µg/L)
0
10
20
30
40
50
60
Days
M. hirsuta
ENV494M
ENV425
Killed


Screening Study Microcosms
2500.00
2000.00
1500.00
1000.00
500.00
0.00
MEEPS (µg/L)
0
10
20
30
40
50
60
Days
ENV494M-methane
ENV425-propane
ENV493-isobutane
Killed ENV493-isobutane