National Institute of Environmental Health Sciences
Your Environment. Your Health.

Utilizing Innovative Materials Science Approaches to Enhance Bioremediation

SRP Progress in Research Webinar Session I: PFAS

Synergistic Material-Microbe Interface towards Faster, Deeper, and Air-tolerant Reductive Dehalogenation

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University of California, Los Angeles

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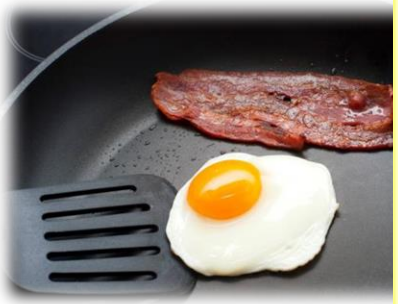
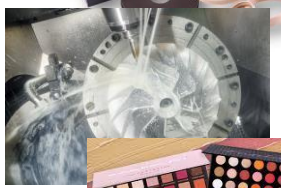
UC RIVERSIDE

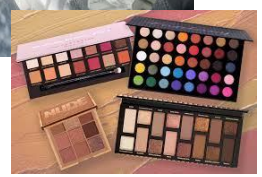
UCLA

Per- and polyfluoroalkyl Substances (PFAS)

$-CF_3$ or $-CF_2-$







Perfluoroalkyl acids and perfluoroalkylether acids (PFAA), e.g.

- **perfluoroalkyl carboxylic acids (PFCA)**, C_nF_{2n+1}-COOH, e.g. PFOA
- **perfluoroalkane sulfonic acids (PFSA)**, C_nF_{2n+1}-SO_3H, e.g. PFOS
- **perfluoroalkyl phosphonic acids (PFPA)**, C_nF_{2n+1}-PO_3H_2
- **perfluoroalkyl phosphinic acids (PFPiA)**, $(C_nF_{2n+1})(C_mF_{2m+1})$-$PO_2H$
- **perfluoroalkylether carboxylic acids (PFECA)**, e.g. $C_2F_5OC_2F_4OCF_2COOH$
- **perfluoroalkylether sulfonic acids (PFESA)**, e.g. $C_6F_{13}OCF_2CF_2SO_3H$

Precursors to PFAA, e.g.

- **perfluoroalkane sulfonyl fluoridess (PASF)**
- **perfluoroalkanoyl fluorides (PACF) and their derivatives**, $C_nF_{2n+1}SO_2$-R / $C_nF_{2n+1}CO_2$-R
- **n:2 fluorotelomer-based substances** $C_nF_{2n+1}CH_2CH_2$-R
- **per- and polyfluoroalkylether-based substances** e.g. $C_nF_{2n+1}OC_mF_{2m+1}$-R

→ **side-chain fluorinated polymers** e.g. (meth)acrylate, urethane, or oxetane polymers with non-fluorinated backbones and fluorinated side-chains

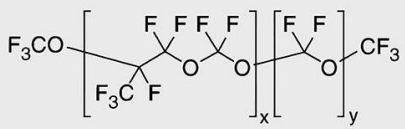
→ **non-polymers** R = NH, $NHCH_2CH_2OH$, etc.

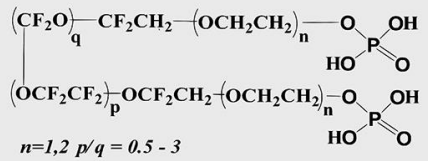
some hydrofluorocarbons (HFCs, e.g. C_nF_{2n+1}-C_mH_{2m+1}), **hydrofluoroethers (HFEs**, e.g. $C_nF_{2n+1}OC_mH_{2m+1}$) and **hydrofluoroolefins (HFOs**, e.g. C_nF_{2n+1}-$CH=CH_2$);
perfluoroalkyl ($C_nF_{2n+1}C(O)C_mF_{2m+1}$) and **semi-fluorinated** ($C_nF_{2n+1}C(O)C_mH_{2m+1}$) **ketones;**
perfluoroalkyl alcohols ($C_nF_{2n+1}OH$)

Fluoropolymers, e.g.

- polytetrafluoroethylene (**PTFE**), $-(CF_2CF_2)_n-$
- polychlorotrifluoroethylene (**PCTFE**), $-(CF_2CFCl)_n-$
- polyvinylidene fluoride (**PVDF**), $-(CF_2CH_2)_n-$
- fluorinated ethylene propylene (**FEP**), $-(CF_2CF_2)_n-(CF_2C(CF_3)F)_m-$

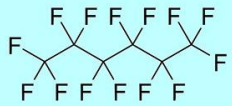
Perfluoropolyethers, e.g.



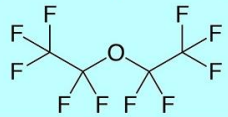


Other PFAS*, e.g.

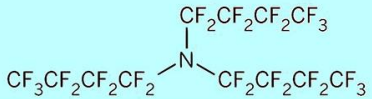
perfluoroalkanes, e.g.



perfluoroalkylethers, e.g.



perfluoroalkylamines, e.g.

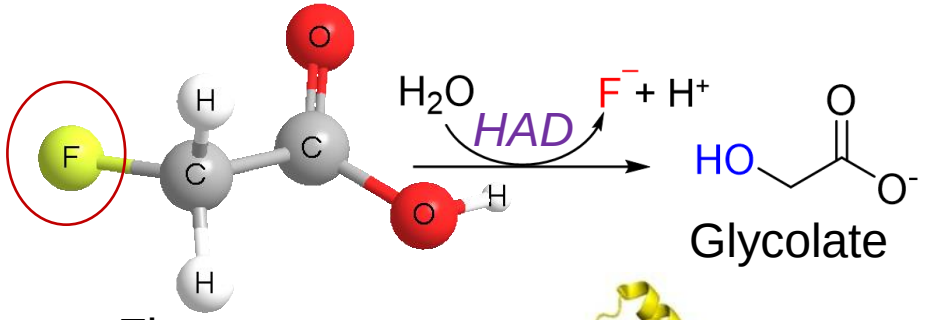


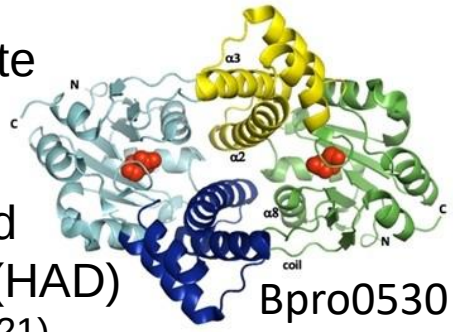
* These PFAS have been less discussed in the public domain, but they meet the definition of PFAS as recommended in Buck et al. (2011) and OECD (2018). They are primarily PFAS with limited chemical reactivity.

(Kwiatkowski et al., 2020. ES&T Lett.; Wang et al., 2021. ES&T)

Microbial Cleavage of C–F bonds

Nature-made organofluorines (biologically)





L-2-haloacid dehalogenases (HAD)
(Chan et al., 2021)

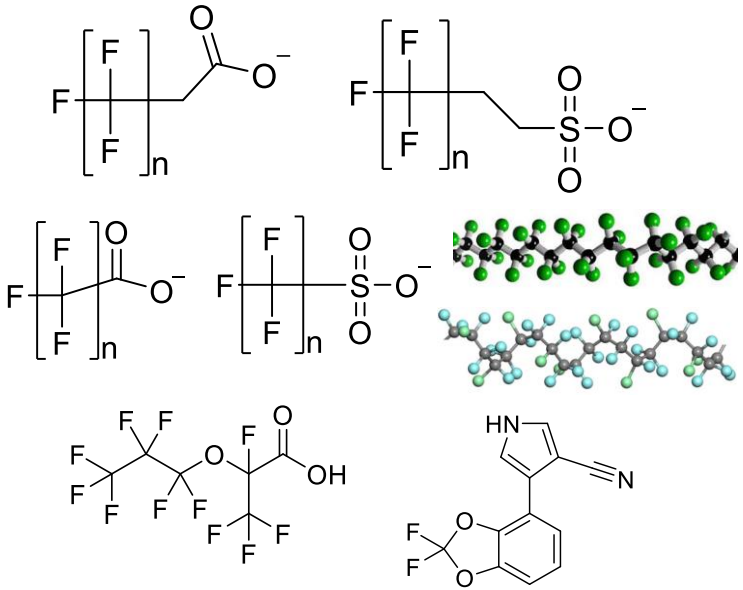
Bpro0530

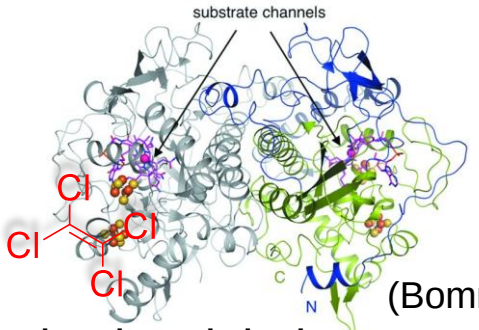
Fact sheet

- The strongest single bond
- The highest electronegativity
- Much lower redox potential (reaching the physiological limit)
- Toxicity of intracellular F^-

(Wackett, 2021; Gribble, 2002; Park *et al.*, 2009)

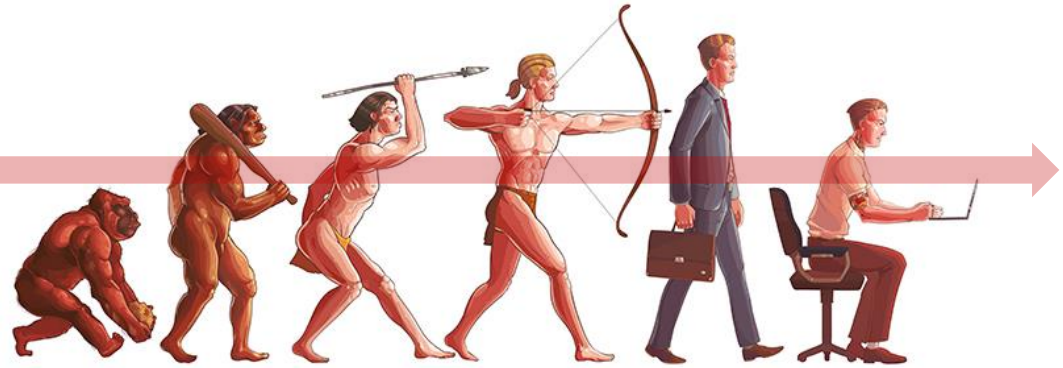
Man-made organofluorines



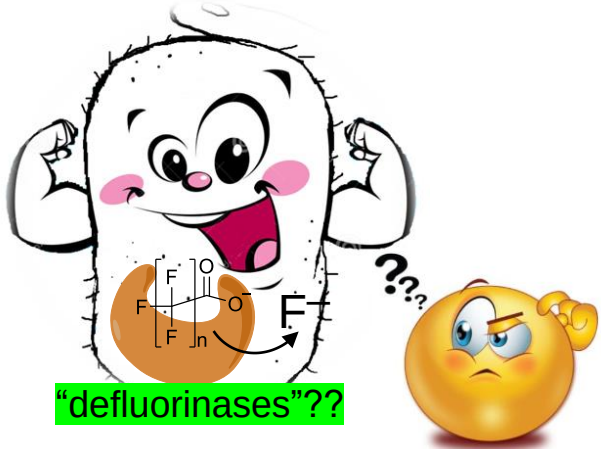


(Bommer et al., 2014)

Reductive dehalogenases

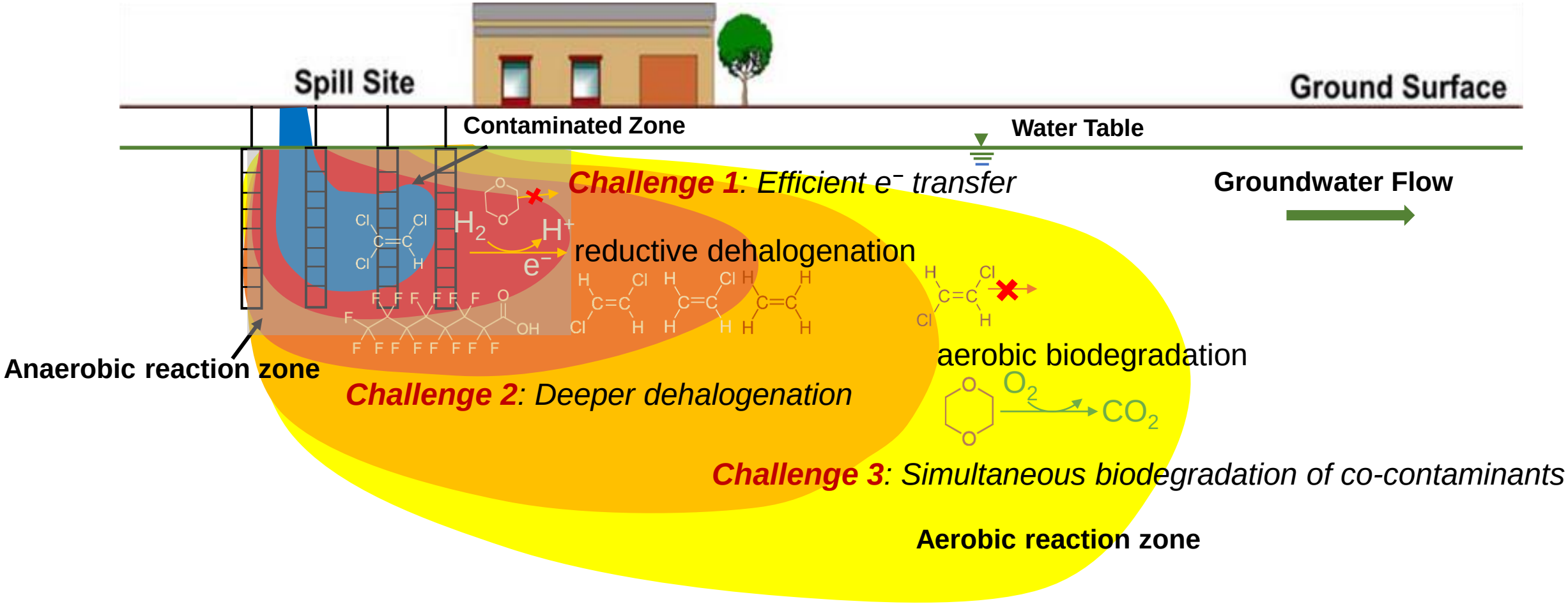


(Picture source: google.com)



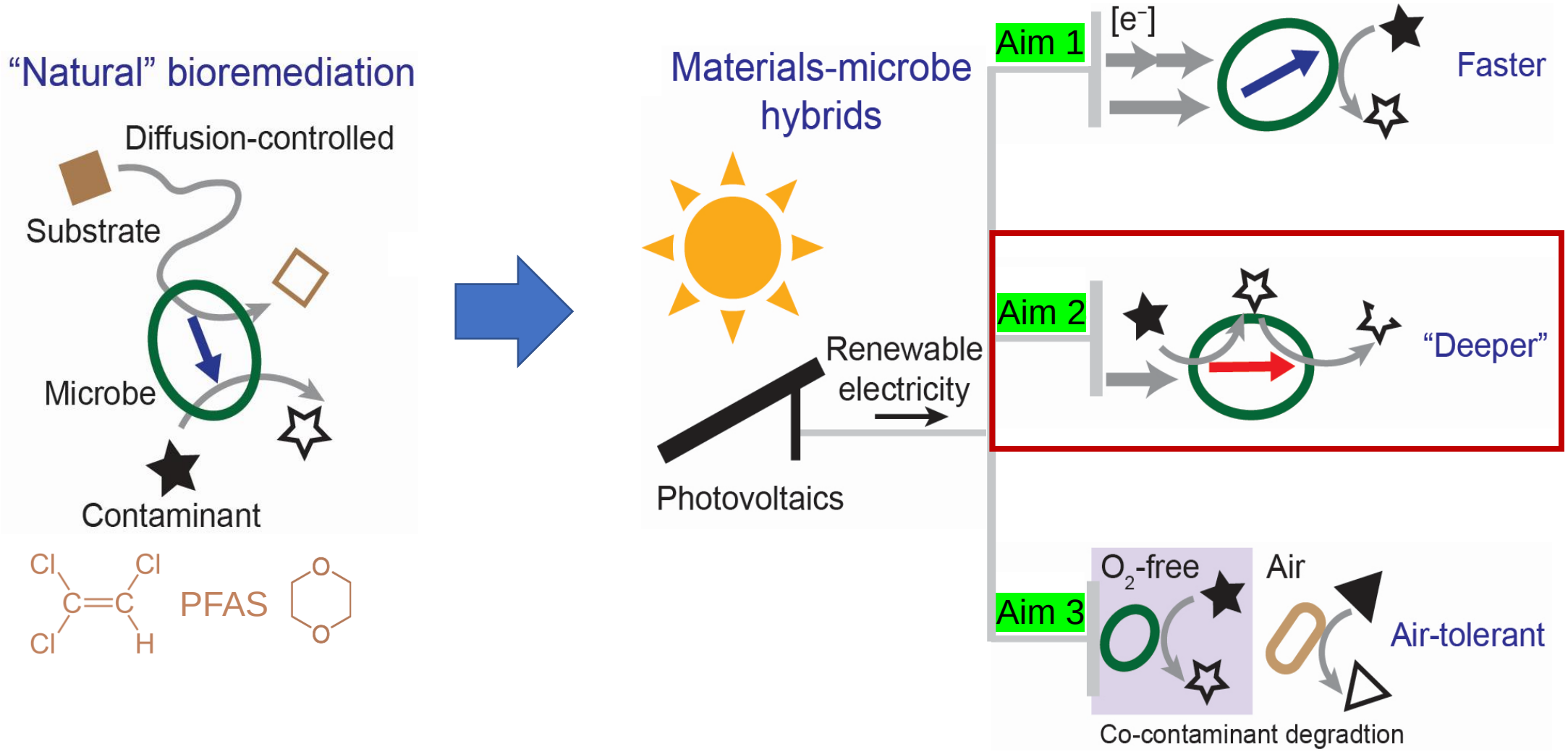
"defluorinases"??

Bioremediation of halogenated contaminants and co-contaminants

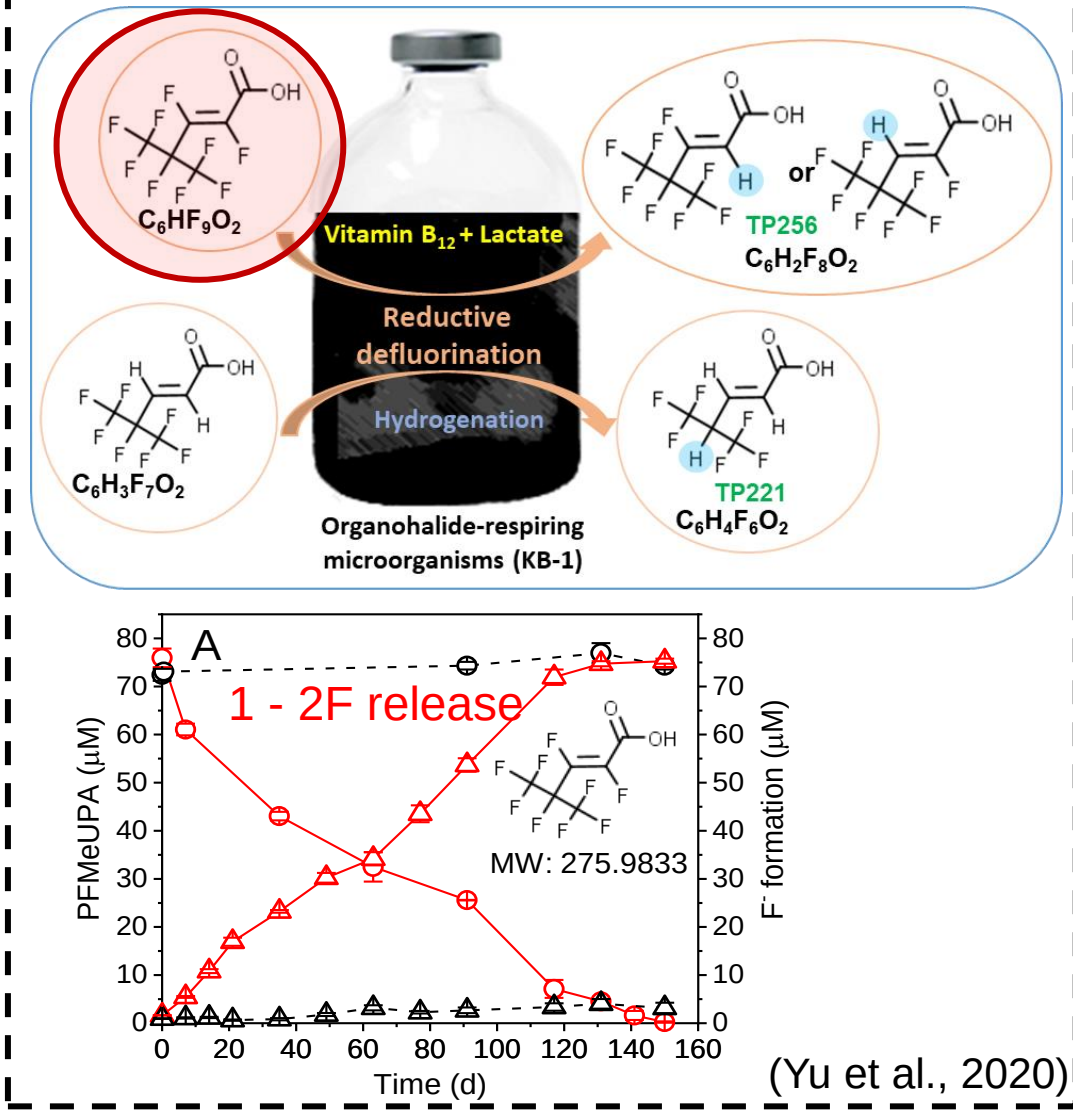


- The goal: address the bioremediation challenges using ***a synergistic materials-microbe interface***

Synergistic Material-Microbe Interface towards Faster, Deeper, and Air-tolerant Reductive Dehalogenation

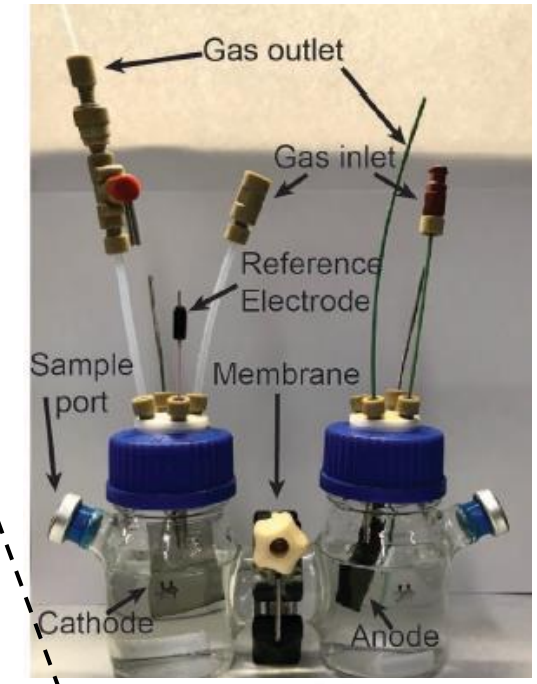


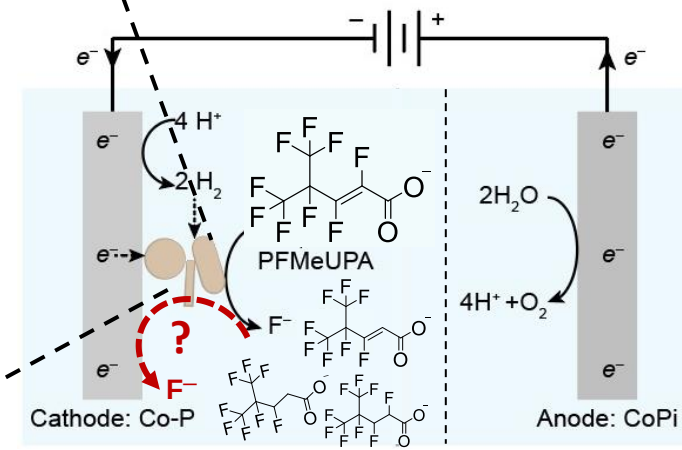
Biological reductive defluorination



(Yu et al., 2020)

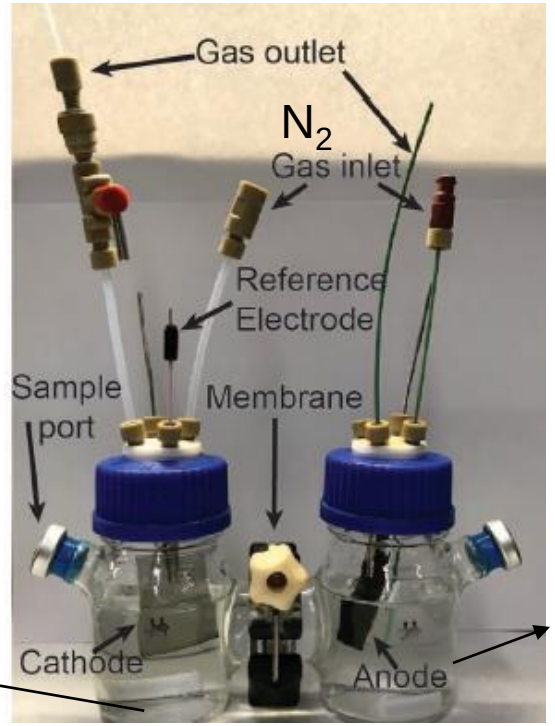
Bioelectrochemical reductive defluorination





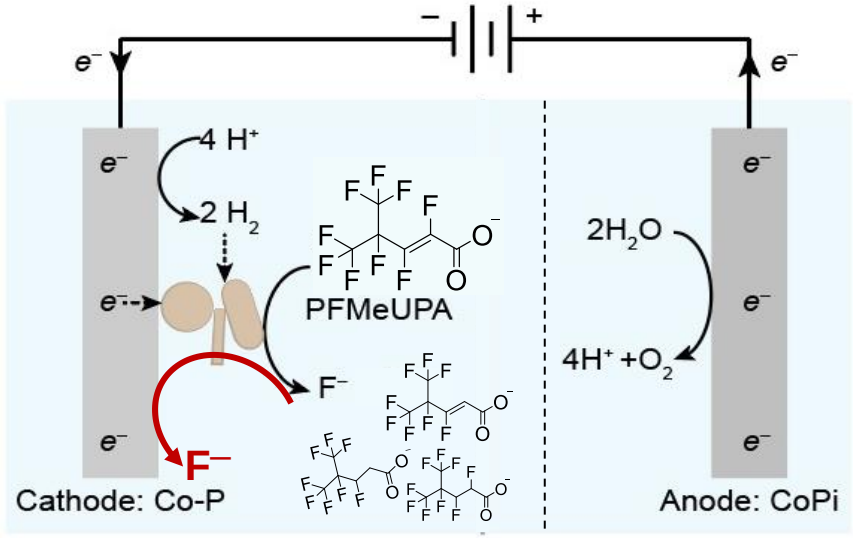
Questions

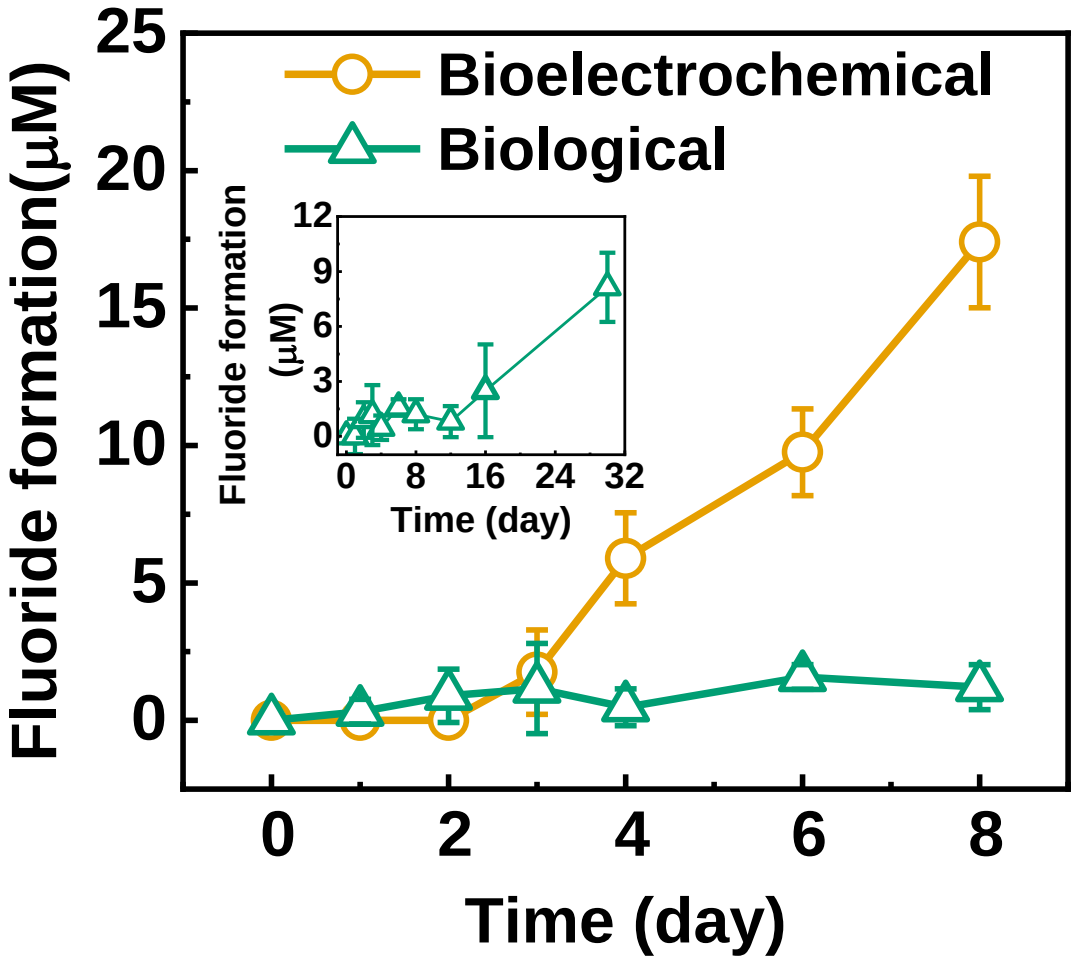
- Can biodefluorination be enhanced in the electrochemical system?
- And if so, via which mechanisms?
  - Enhanced biodefluorination by enhanced e⁻ transfer?
  - Synergies between biological and electrochemical defluorination?

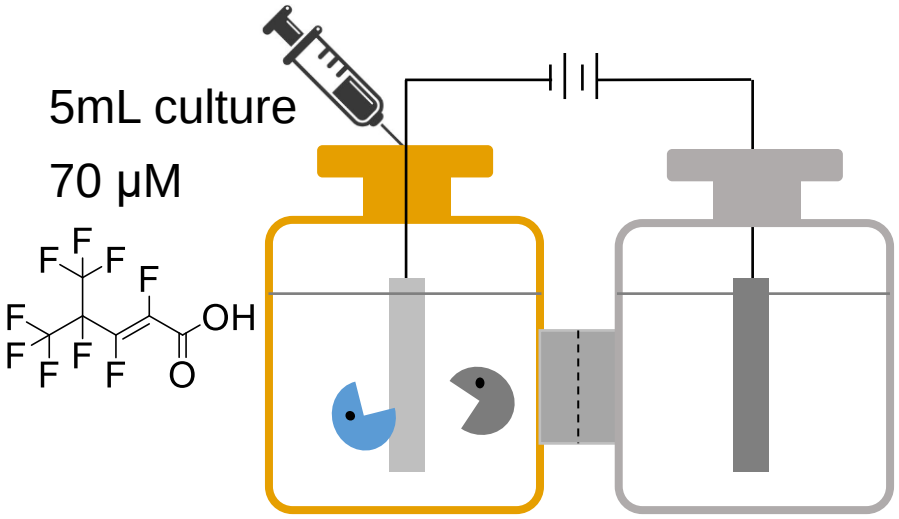


5 mL culture in 95 mL medium 70 μM PFMeUPA

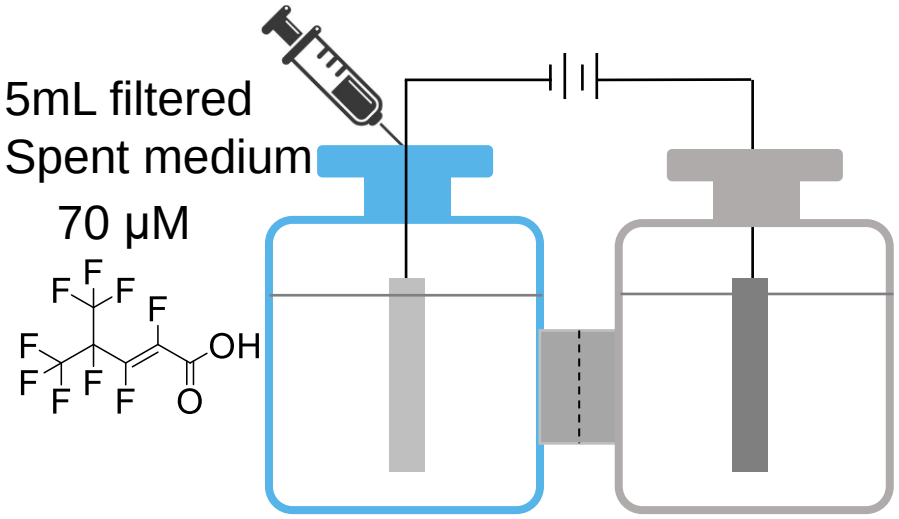
100 mL basal medium



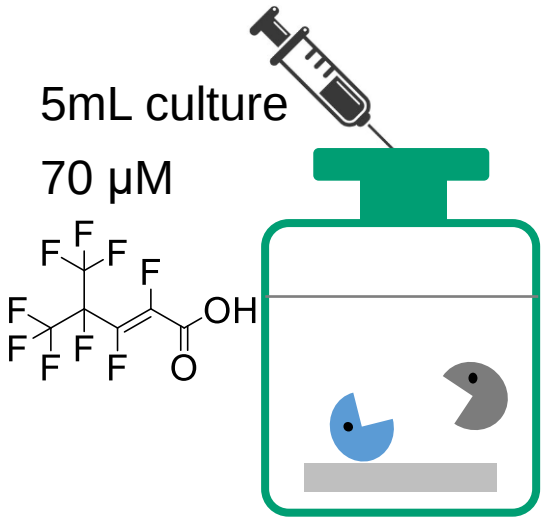




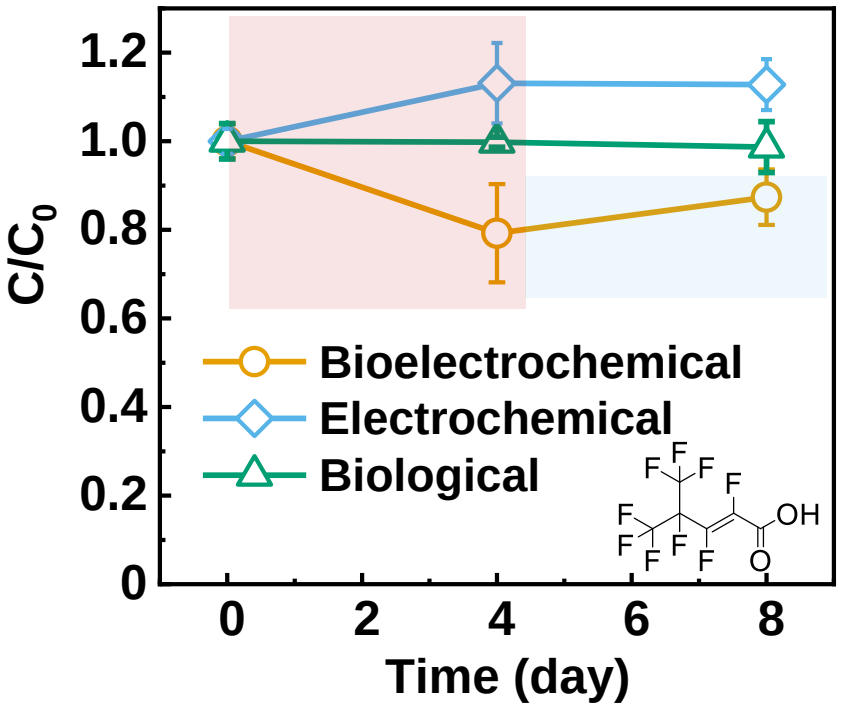
Bioelectrochemical



Electrochemical



Biological

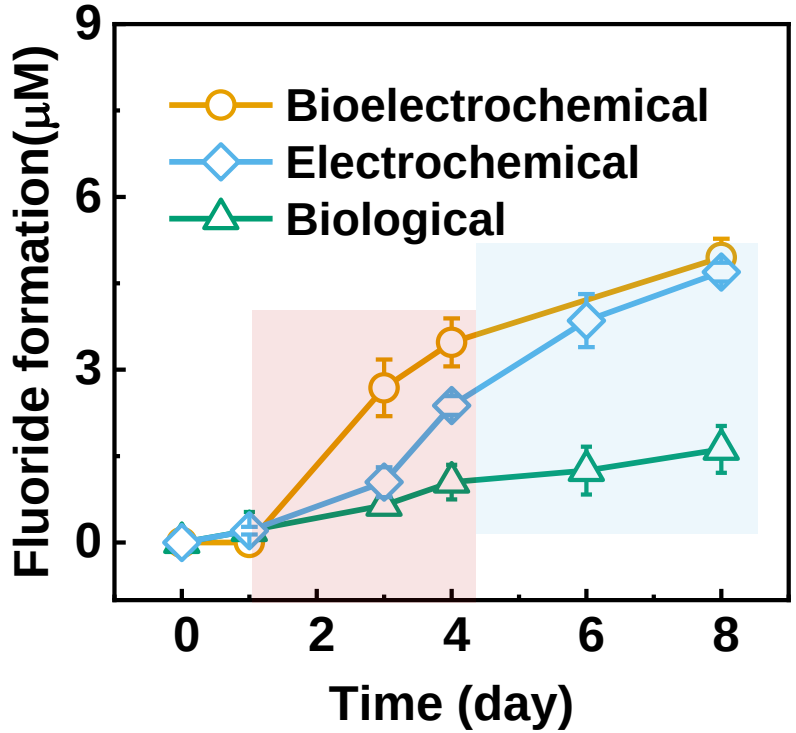


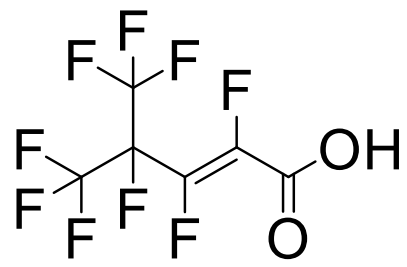
- Parent compound:

  Biodefluorination only

- Biodefluorination intermediates:

  Electrochemical or Bioelectrochemical



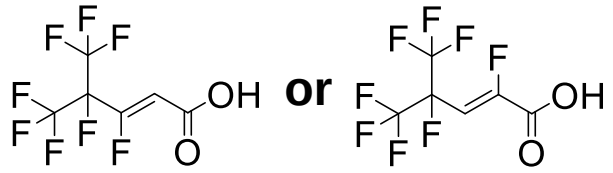


PFMeUPA($C_6HF_9O_2$)^{CL1}

CL: confidence level

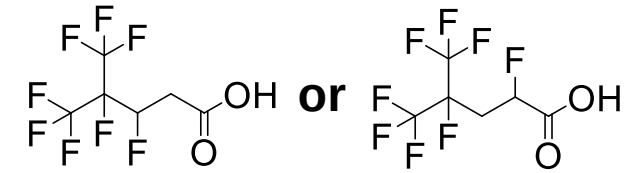
–F,+H

+2H

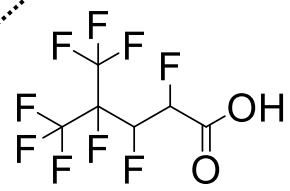


TP256($C_6H_2F_8O_2$) ^{CL2b}

+2H



TP259($C_6H_4F_8O_2$) ^{CL2b}

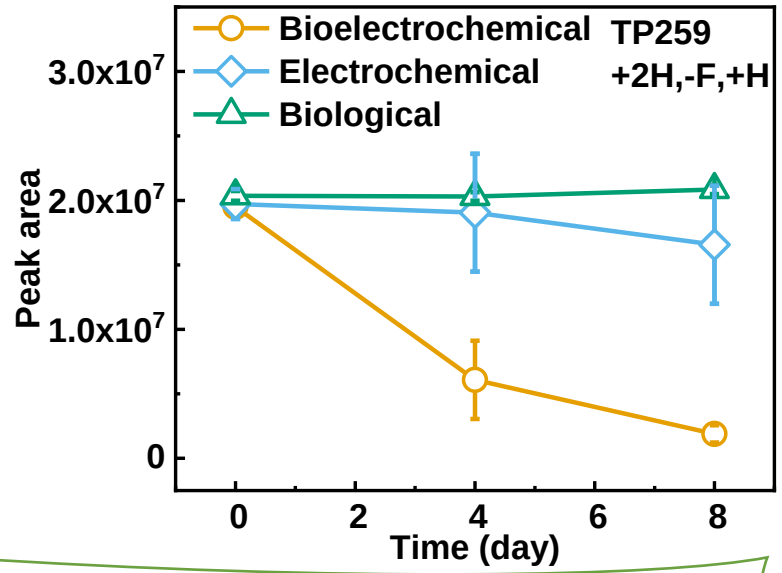


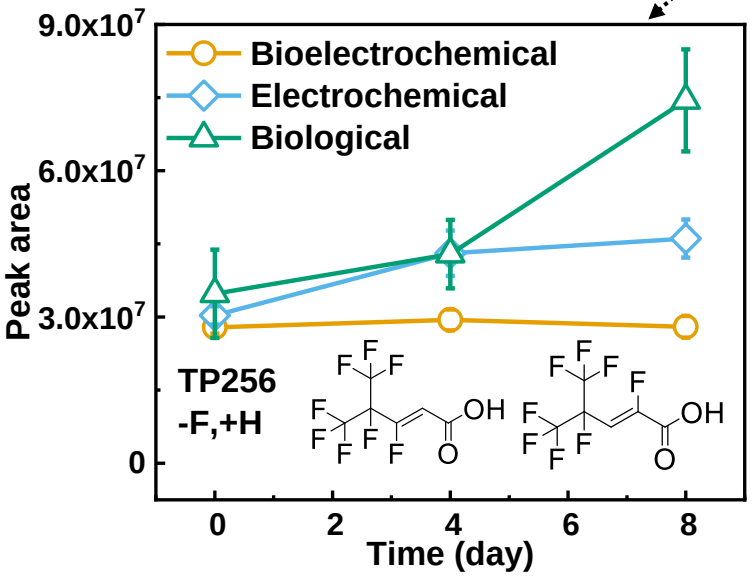
TP276($C_6H_3F_9O_2$) ^{CL2b}

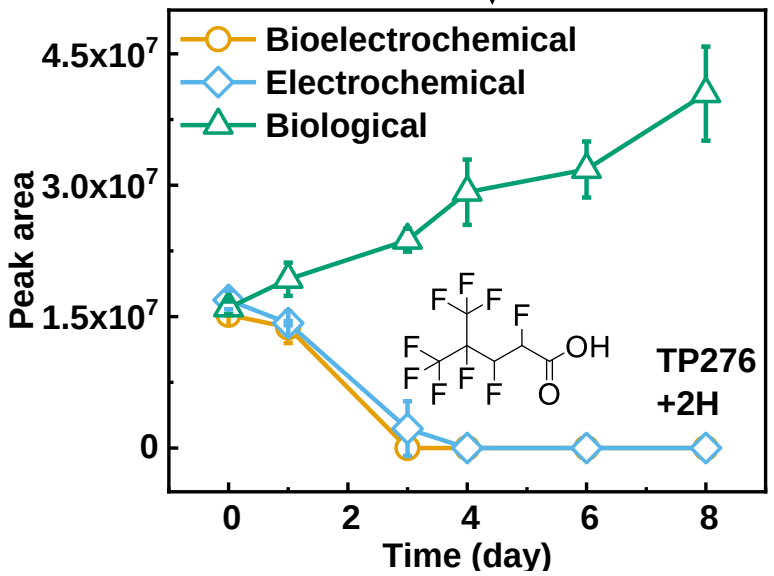
–HF

–F,+H

Biological system







TP Identification Criteria

- Peak area > 10^5
- Isotopic pattern score > 70
- Formation trend
- Not in-source fragment

Biodefluorination

Electrochemical defluorination

PFMeUPA($C_6HF_9O_2$)^{CL1}

CL: confidence level

–F,+H

+2H

TP256($C_6H_2F_8O_2$) CL2b

+2H

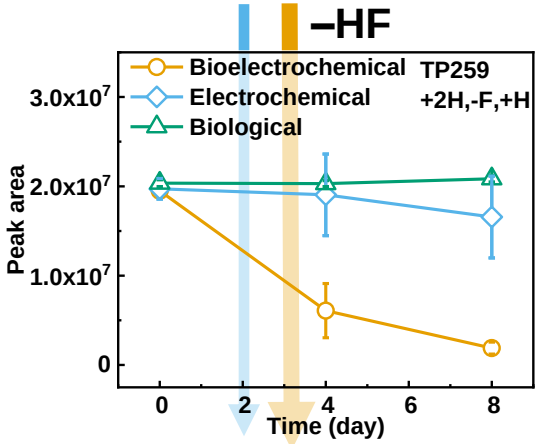
TP259($C_6H_4F_8O_2$) CL2b

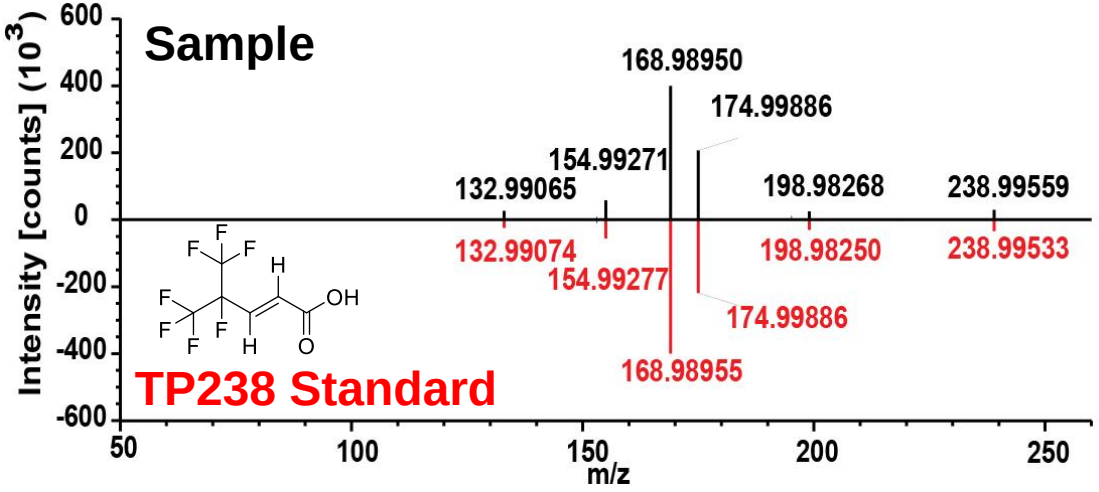
–HF

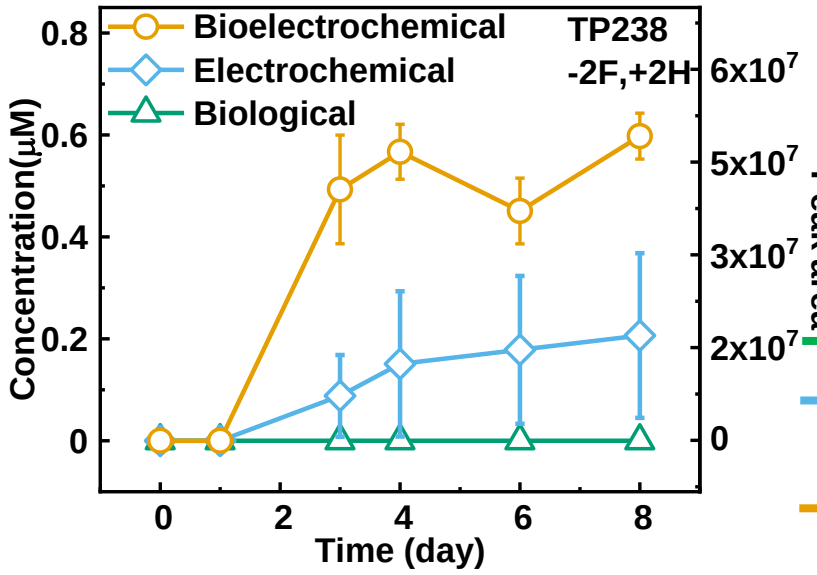
TP276($C_6H_3F_9O_2$) CL2b

–F,+H

Biological system





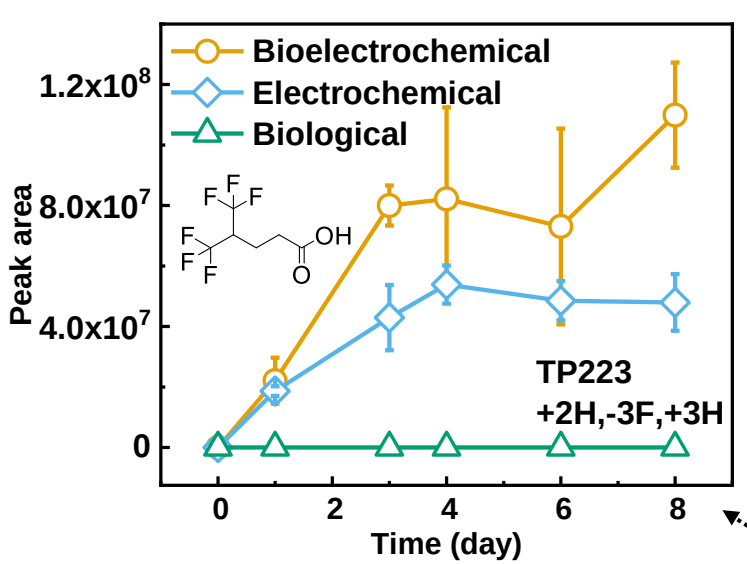


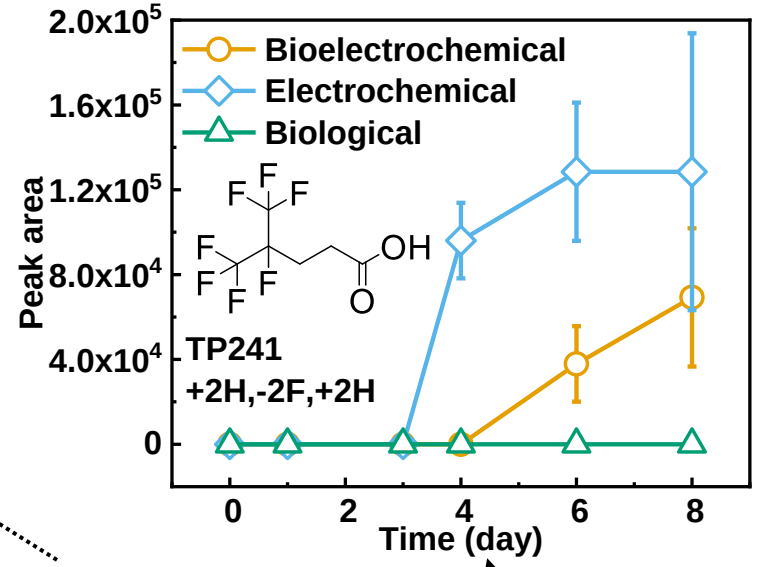
TP238($C_6H_3F_7O_2$)^{CL1}

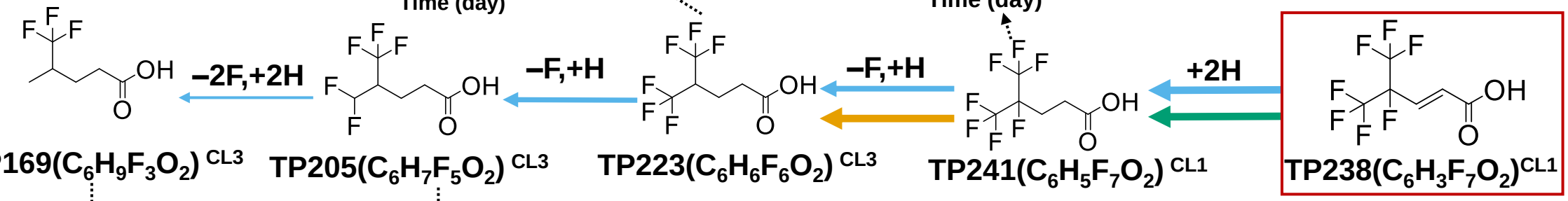
Biodefluorination

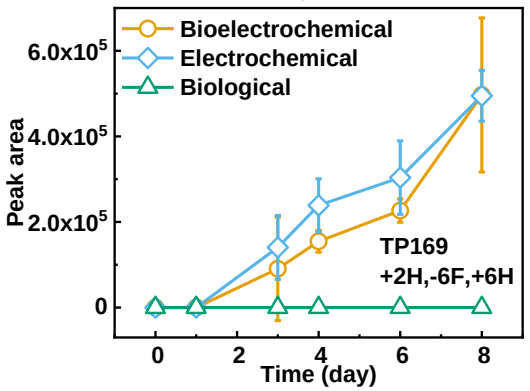
Electrochemical defluorination

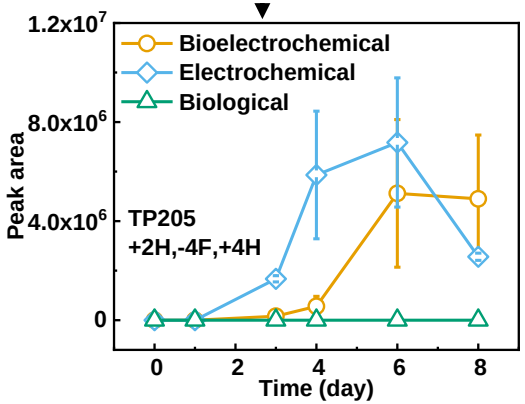
Bioelectrochemical defluorination

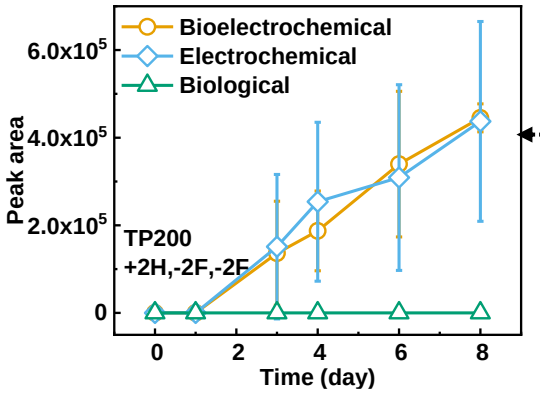


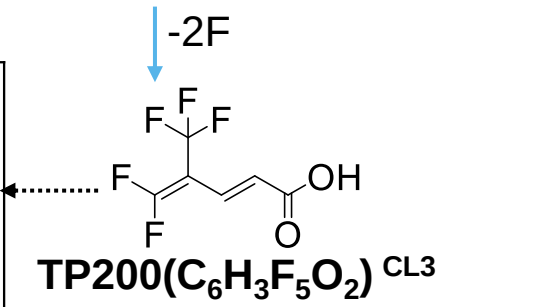




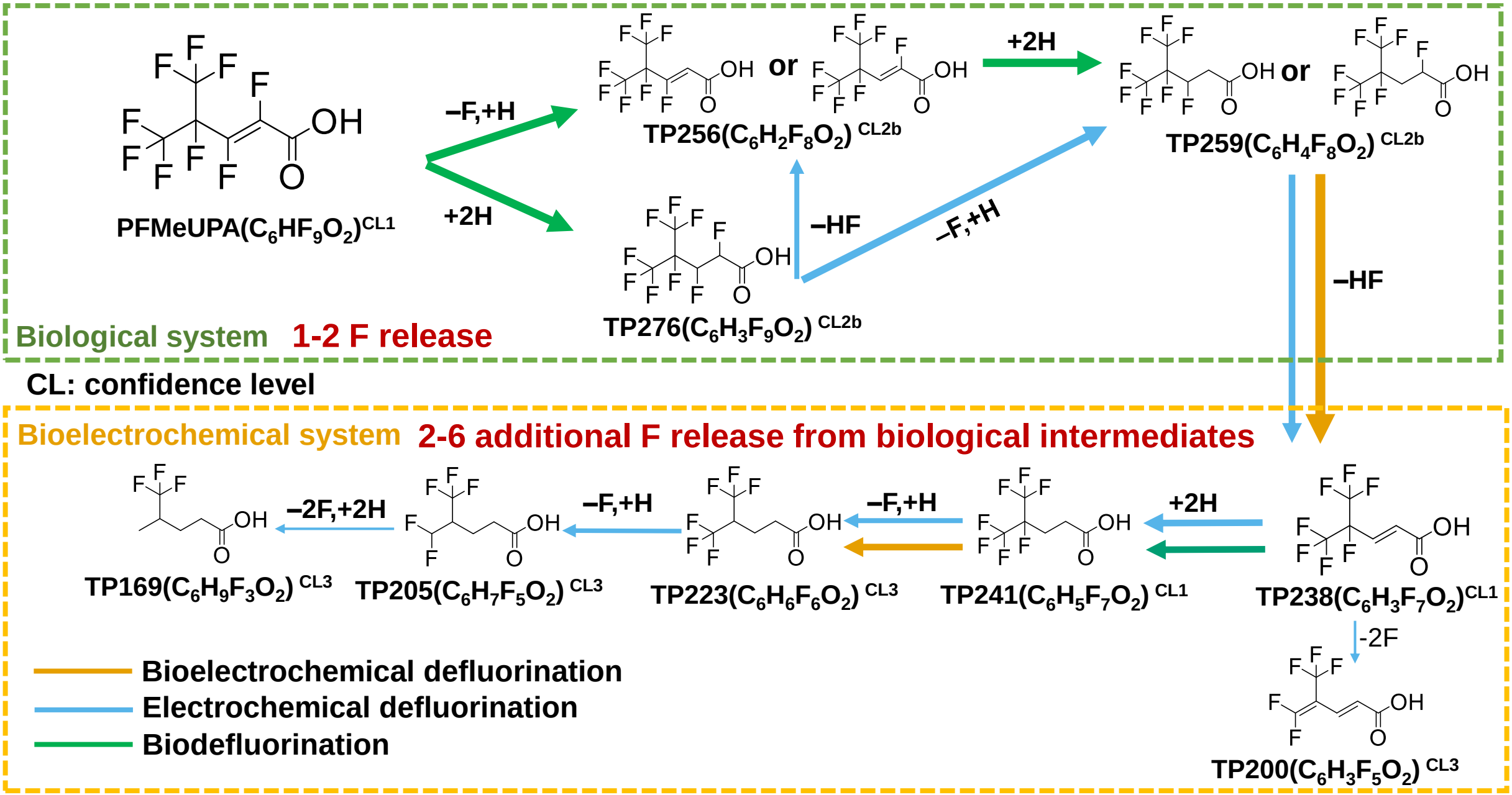






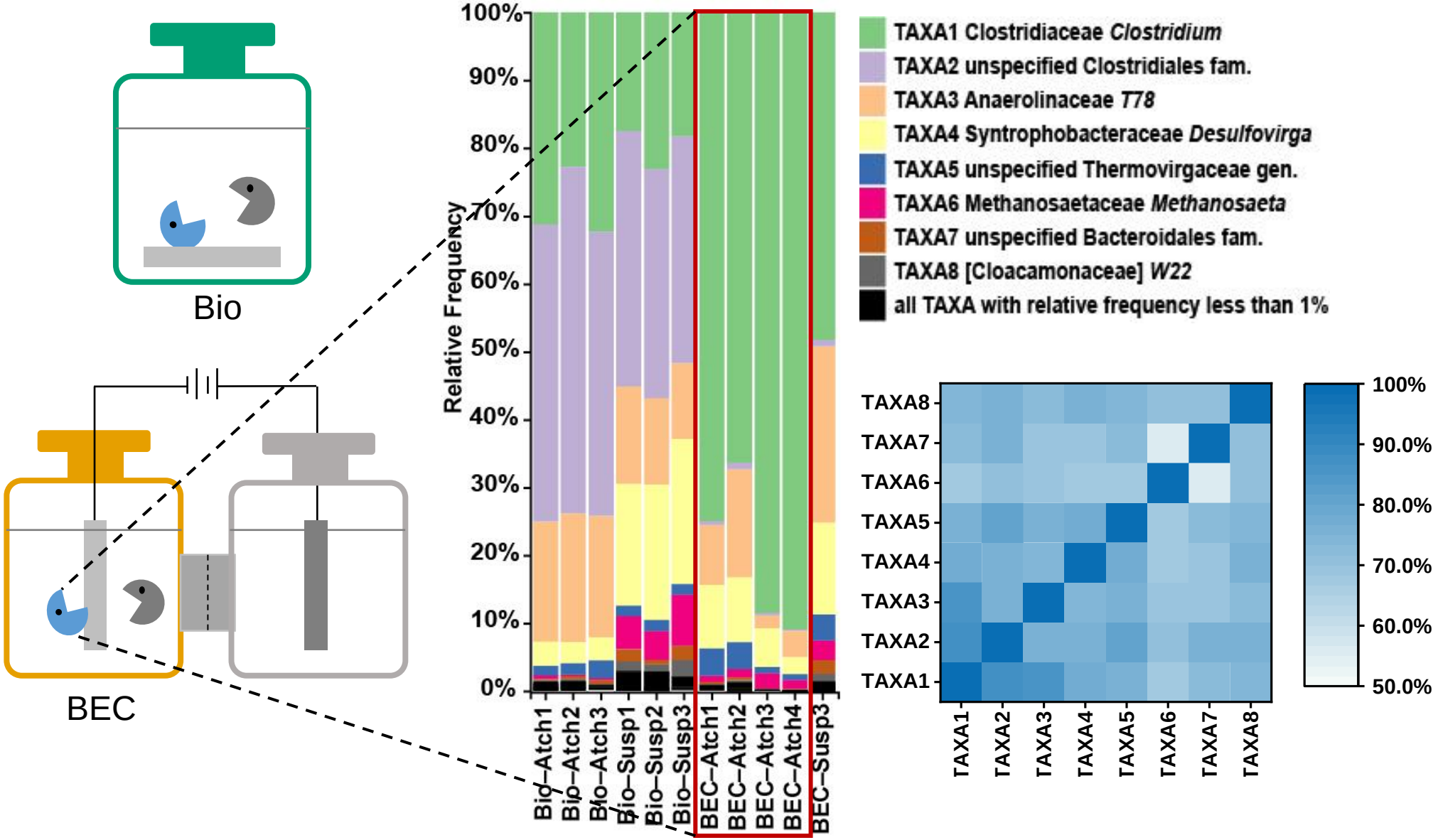


Biological
Electrochemical
Bioelectrochemical



Che et al., *in prep*

Microbial community change in the bioelectrochemical system



Questions

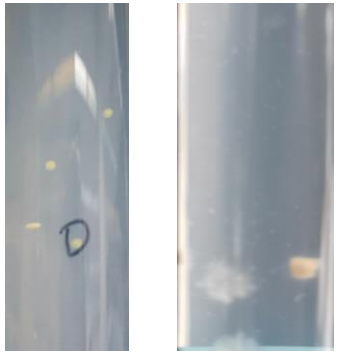
- Can biodefluorination be enhanced in the electrochemical system?
- And if so, via which mechanisms?
  - Enhanced biodefluorination by enhanced e^- transfer?
  - Synergies between biological and electrochemical defluorination?

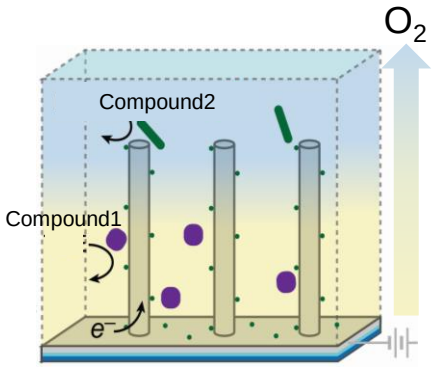
Take-home Messages

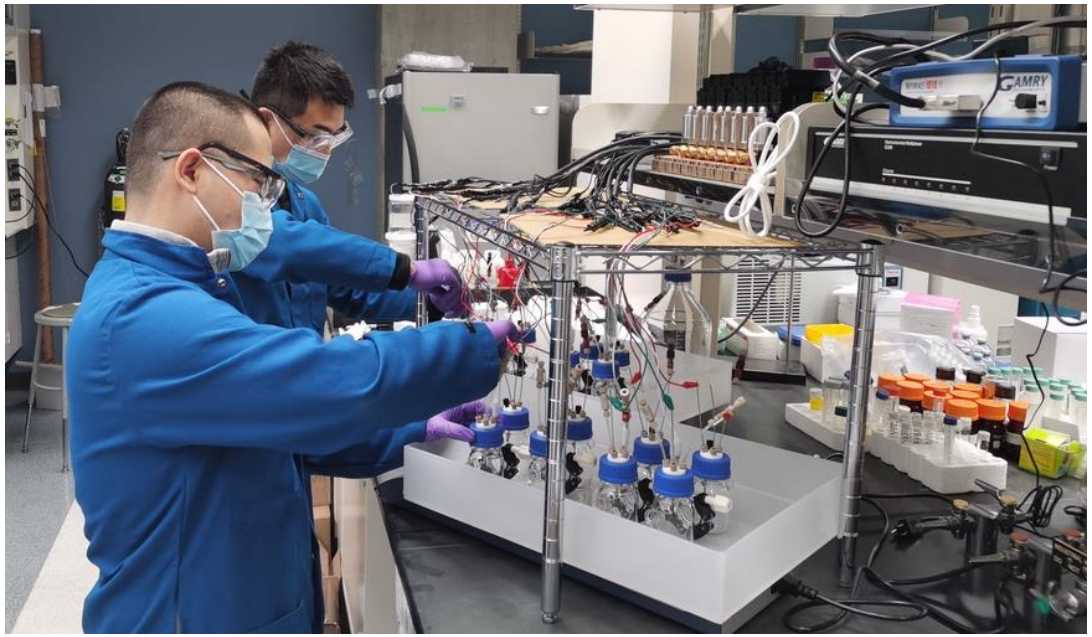
- Faster and deeper reductive defluorination was achieved in the bioelectrochemical system.
- The mechanic understanding:
  - The synergies between biodefluorination of the parent compound and electrochemical defluorination of the biodefluorination products.
  - The electrochemically facilitated biodefluorination of intermediates.

Ongoing work

- Optimize the electrochemical system to better support sustainable growth of the defluorinating culture.
- Integration of other novel nanomaterials to further enhance defluorination.
- Test different PFAS compounds.
- Test different defluorinating cultures obtained in the lab and from other labs.







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Interested?

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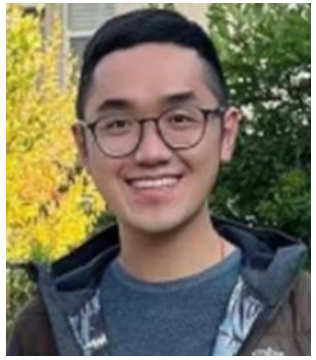
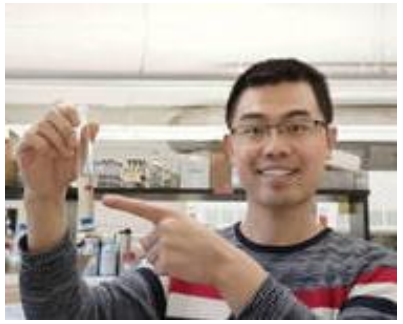
Acknowledgements

Shun Che



Dr. Yaochun Yu (former)



Dr. Huaqing Liu (former)

David Alfaro (Rotation PhD student

Collaborators/Stakeholders

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Dr. Jeff Roberts
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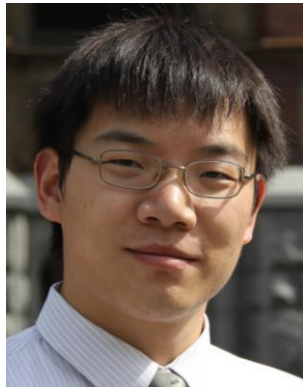

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