Microbial Defluorination of Unsaturated Per- and Polyfluorinated Carboxylic Acids under Anaerobic and Aerobic Conditions: A Structure Specificity Study

Yaochun Yu (yyu54@illinois.edu) and Shun Che (University of California, Riverside, Riverside, CA, USA; University of Illinois at Urbana-Champaign, Urbana, IL, USA)
Changxu Ren and Bosen Jin (University of California, Riverside, Riverside, CA, USA)
Zhenyu Tian (Northeastern University, Boston, MA, USA)
Sandra Dworatzek, Jennifer Webb, and Jeff Roberts (SiREM, Guelph, ON, Canada)
Jinyong Liu (University of California, Riverside, Riverside, CA, USA)
Yujie Men (ymen@engr.ucr.edu) (University of California, Riverside, Riverside, CA, USA; University of Illinois at Urbana-Champaign, Urbana, IL, USA)

Background/Objectives. The recently discovered microbial reductive defluorination of two C6 branched and unsaturated fluorinated carboxylic acids (FCAs) provided valuable insights into the environmental fate and potential bioremediation strategies of per- and polyfluoroalkyl substances (PFAS). However, a systematic investigation is needed to further demonstrate the role of C=C double bonds in the bioavailability of unsaturated PFAS in both anaerobic and aerobic environments. Here, we examined the structure-bioavailability relationships of thirteen FCAs, including nine commercially available unsaturated FCAs and four structurally similar saturated ones, by a reductively defluorinating enrichment and activated sludge communities.

Approach/Activities. Anaerobic defluorinating enrichment originated from a commercial bioaugmentation culture and was maintained in a mineral salts medium amended with vitamin B_{12}, reducing agents, lactate (the primary electron donor), and the unsaturated and branched PFAS (the electron acceptor), which have been reported to be defluorinated by the enrichment. The aerobic activated sludge community was taken from a local municipal wastewater treatment plant. The transformation products were analyzed by high-resolution mass spectrometry to elucidate the reaction pathways, and fluoride ion concentration was measured to determine the overall defluorination percentage.

Results/Lessons Learned. The results showed that under anaerobic conditions, the α, β-unsaturation is crucial for FCA biotransformation via reductive defluorination and/or hydrogenation pathways. With sp^2 C-F bonds being substituted by C-H bonds, the reductive defluorination became less favorable than hydrogenation. Moreover, for the first time, we reported enhanced degradability and defluorination capability of specific unsaturated FCA structures with trifluoromethyl ($–CF_3$) branches at the α/β-carbon. Such FCA structures can undergo anaerobic abiotic defluorination in the presence of reducing agents and significant aerobic microbial defluorination. Given the diverse applications and emerging concerns of fluorochemicals, this work not only advances the fundamental understanding of the fate of unsaturated PFAS in natural and engineered environments but may also provide important insights into the design of readily degradable fluorinated alternatives to existing PFAS compounds.