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Letter

Structure-Specific Aerobic Defluorination of Short-Chain Fluorinated Carboxylic Acids by Activated Sludge Communities

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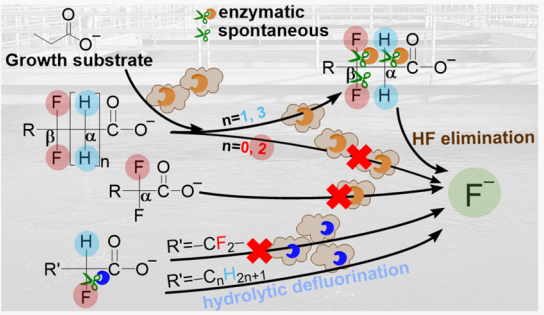
ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are a large group of manmade chemicals that impose emerging environmental concerns. Among them, short-chain per- and polyfluorinated carboxylic acids represent an important subgroup used as building blocks of biologically active chemicals and functional materials. Some are also considered PFAS alternatives, and some could be byproducts of the physicochemical treatment of PFAS. However, little is known about the environmental fate of short-chain fluorinated carboxylic acids (FCAs) and their defluorination/transformation by microorganisms. To fill the knowledge gap, we investigated the structure−reactivity relationships in the aerobic defluorination of C_3−C_5 FCAs by activated sludge communities. Four structures exhibited greater than 20% defluorination, with 3,3,3-trifluoropropionic acid being almost completely defluorinated. We further analyzed the defluorination/transformation pathways and inferred the structures susceptible to aerobic microbial defluorination. We also demonstrated that the defluorination was via cometabolism. The findings advance the fundamental understanding of aerobic microbial defluorination and help assess the environmental fate of PFAS. Since some short-chain PFAS, such as 3,3,3-trifluoropropionic acid, are the incomplete defluorination byproducts of advanced reduction processes, their defluorination by activated sludge communities sheds light on the development of cost-effective chemical−biological PFAS treatment train systems.



INTRODUCTION

Organofluorines, particularly per- and polyfluoroalkyl substances (PFAS), have caused a rapidly growing concern in public health and ecosystems.[1−6] Short-chain PFAS are synthesized as important building blocks and intermediates of biologically active compounds and functional materials.[7−9] Also, as long-chain legacy PFAS have led to increasing regulatory attention, structurally similar short-chain PFAS have been adopted as alternatives for commercial manufacturing.[1] Meanwhile, some short-chain PFAS may be formed as the incomplete defluorination byproducts during physicochemical treatment of PFAS[10−12] and the biotransformation products of other synthetic organofluorines.[13] The environmental fate, transport, and biotransformation of ≥ C_7 PFAS have been extensively studied.[14−18] Compared to those long-chain ones, shorter-chain PFAS possess higher motility in water and lower adsorption potential to particles, which enable them to easily transport through water bodies and soil in long distance and be detected in increasing presence in aquatic environments.[19,20] However, their biodegradability by environmental microorganisms and activated sludge communities in wastewater treatment plants (WWTPs) is largely unknown.

Given the broad applications and increasing occurrence of short-chain PFAS, we aimed to explore the defluorination of select short-chain fluorinated carboxylic acids (FCAs) by activated sludge communities and determine the structure−reactivity relationship in the aerobic microbial defluorination, hence providing critical fundamental knowledge to assess the environmental fate of short-chain PFAS and guide the design of cost-effective treatment strategies. We investigated 14 commercially available C_3−C_5 FCAs and identified the defluorination pathways of the transformed ones. We further summarized the specific PFAS structures susceptible to aerobic microbial defluorination and discussed the critical implications of our findings to the understanding of the environmental fate of PFAS and the application of biological approaches in treating PFAS.

MATERIALS AND METHODS

Chemicals. The 14 short-chain FCAs (Figure 1A and details in Table S1 and Figure S1) were purchased from SynQuest Laboratories (Alachua, FL).

Biotransformation/Biodefluorination Batch Experiments. Activated sludge samples (~4400 mg/L as mixed liquor suspended solids) were obtained in the aeration tank of a

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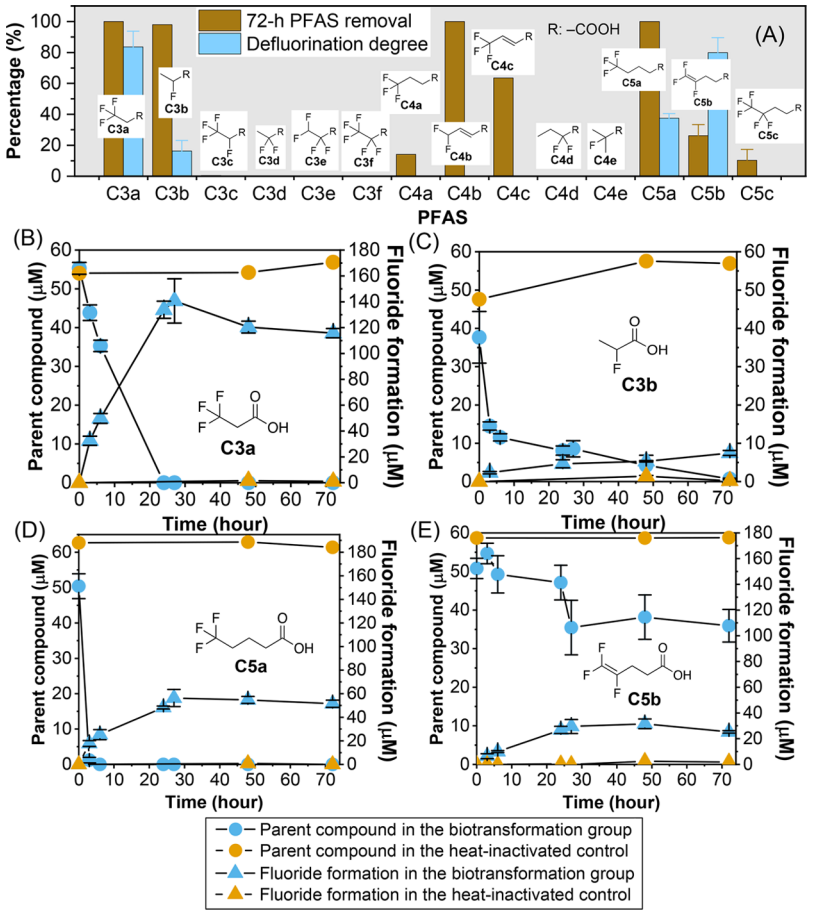

Figure 1. Parent compound removal and defluorination degree of all tested short-chain FCAs after 72 h (A) and temporal parent compound decay and fluoride formation for the four structures with defluorination activities (B, **C3a**; C, **C3b**; D, **C5a**; E, **C5b**; n = 3).

local municipal WWTP the same day of the experiment. The biotransformation experiments were conducted in batch reactors (150 mL, loosely capped) for 3−14 days, with the dissolved oxygen (DO) above 3 mg/L (Figure S2) over 14 days. Each biotransformation reactor contained 50 mL of fresh activated sludge and 50 μM individual FCAs. Heat-inactivated controls were prepared using autoclaved (121 °C, 40 min) sludge filtrate (0.22 μm filter). A no-FCA sludge control reactor was also performed to obtain the sludge matrix and correct the fluoride measurement. Details of the cosubstrate experiment and the activated sludge treatment of the effluent from a photochemical reactor treating perfluoropropionic acid (PFPrA) are described in the Supporting Information.

Triplicated reactors were set up for all the above experiments. The reactors were shaken on an open-air shaker at 150 rpm at room temperature. The culture suspension was sampled (~3 mL) up to 14 days. Sampling after an extended incubation of 14 days was done for structures that did not show significant removal after 72 h (methanol and ammonium were supplied to maintain the sludge activity after 3 days). Samples were centrifuged at 13,000 rpm for 10 min. The supernatant (~2.5 mL) was collected for fluoride quantification and analysis of the parent compound and transformation products. The cell pellets were subject to methanol extraction for analysis of adsorbed and intracellular parent compounds and transformation products (see the detailed procedure in the Supporting Information).

Fluoride Measurement. Fluoride ions were measured using an ion-selective electrode (ISE) (HACH). The quantification limit was 0.01 mg/L (c.a. 0.53 μM). The ISE results were cross-validated using ion chromatography (IC). Details of the two methods are provided in the Supporting Information. The differences between the two were within 10% (Figure S3). The defluorination degree for the removed portion of PFAS was determined using the formula below

$$\text{Defluorination degree}\,(\%) = \frac{\text{Max. fluoride formed}}{\text{Removed PFAS conc.} \times \text{number of F in one molecule}} \times 100\%$$

Analytical Methods. The parent FCAs and transformation product suspects were analyzed by an ultrahigh performance liquid chromatography coupled to a high-resolution quadrupole orbitrap mass spectrometer (UHPLC-HRMS/MS, Q Exactive, Thermo Fisher Scientific, Waltham, MA). Here, a 2 μL sample was injected into a Hypersil Gold column (particle size 1.9 μm, 2.1 mm × 100 mm, Thermo Fisher Scientific) and eluted at 0.30 mL/min with water (A) and methanol (B), each containing 10 mM ammonium acetate. The analytical method details and transformation product analysis are described in the Supporting Information.

RESULTS AND DISCUSSION

Biodefluorination of Short-Chain PFAS by Activated Sludge Communities Was Structure Dependent. We investigated a series of commercially available C_3−C_5 FCAs (14

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Environ. Sci. Technol. Lett. 2021, 8, 668−674

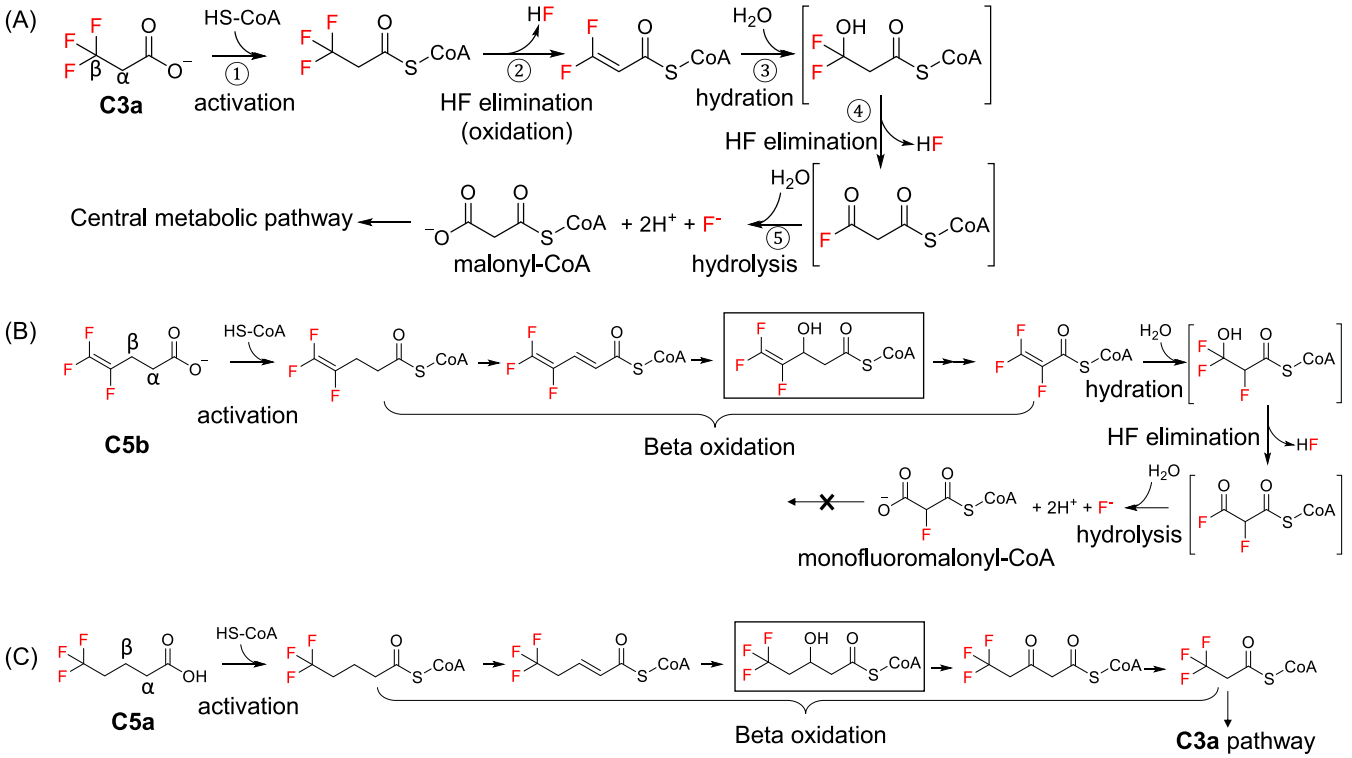

Figure 2. Proposed defluorination pathway of **C3a** (A), **C5b** (B), and **C5a** (C). Note: In the boxes are the proposed intermediates whose hydrolyzed products (the 3-hydroxyl acids) were detected; in brackets are unstable intermediates.

total), which have various fluorine substitution degrees, linear and branched, and saturated and unsaturated structures. Six compounds showed a significant removal (>20%) after 14 days compared to the heat-inactivated abiotic controls (Figure 1A and Figure S4). Slight adsorption or uptake of those compounds was observed on day 0, which was further accumulated and accounted for less than 10% of the total amount after 3 days (Figure S5). For **C3a**, **C3b**, and **C5a**, the bioaccumulated portion was depleted after 3 days, consistent with their complete removal. Two C_3 structures (**C3a** and **C3b**) and two C_5 structures (**C5a** and **C5b**) showed significant microbial defluorination with a maximum fluoride formation of greater than 10 μM after a 3-day incubation, compared to a nearly zero fluoride formation in the heat-inactivated control (Figure 1B–E). The other structures did not exhibit defluorination (<6%) even after 14 days. Although not being defluorinated, **C4b** and **C4c** were biotransformed (Figure 1A).

According to Figure 1A, the C–H bonds at the α-carbon seemed to facilitate the initial microbial attack. **C3a** with $-CH_2-$ at the α-position achieved a much higher defluorination degree than **C3b** with one fluorine substitution at the α-position. **C3d** and **C3e** with two α-fluorine substitutions did not show any defluorination activity. The defluorination inefficiency of **C4d** and **C4e** also likely resulted from the lack of C–H bonds at the α-position. Interestingly, different from **C3a** and **C5a**, the C_4 structure with $-CH_2-$ at the α-position (**C4a**) did not show any defluorination activity. The slight 72 h removal (~14%) was largely due to the adsorption (~10%) and evaporation (~6%) (Figure S4). The removal increased to 20% after 14 days, which could be due to continuing adsorption/cell uptake. Even if a small amount of **C4a** could undergo β-oxidation, trifluoroacetate will be the product, which cannot be defluorinated.[21] In contrast, the β-oxidation of **C5a** could form **C3a**, which could be defluorinated. This implies that microbial aerobic defluorination was more likely to occur for odd-chain structures similar to **C5a** ($CF_3(CH_2)_{n-2}COOH$) than even-chain ones. Neither the C=C double bond in **C4c** nor the single H substitution at the $-CF_3$ in **C4b** changed the defluorination inefficiency of **C4a**. However, the two structures did exhibit significantly higher removal via nondefluorinating pathways.

Additionally, the degree of fluorine substitution affected the microbial defluorination at the α-position. For instance, **C3b** and **C3c** both have one α-fluorine substitution, but **C3c** with $-CF_3$ in place of $-CH_3$ in **C3b** was not microbially defluorinated (Figure 1A). It seems that the 2-haloacid **C3b** underwent hydrolytic defluorination, which can be catalyzed by 2-haloacid dehalogenases.[22] If so, the additional fluorine substitutions in **C3c** might negatively affect the substrate affinity of 2-haloacid dehalogenases, rendering no defluorinating activity. Perfluorinated compounds (C_4–C_8) are known to be recalcitrant to aerobic biotransformation;[23−25] thus, it was within our expectation that **C3f** was not defluorinated. Significant biotransformation/biodefluorination was observed for **C5a** and **C5b** but not for **C5c** with two more fluorine substitutions.

Defluorination/Transformation Pathways. We further examined the defluorination pathways of the four defluorinated structures. On the basis of the defluorination degree and identified β-oxidation intermediates, we proposed β-oxidation-like pathways for **C3a**, **C5a**, and **C5b**, using the initial step of typical β-oxidation (HS–CoA activation) (Figure 2). Since no intermediates containing –S–CoA were identified, further evidence will be needed in future studies to validate the proposed pathway. The 3,3,3-trifluoropropionic acid (**C3a**) exhibited the highest defluorination degree (84% ± 10%), suggesting that the three C–F bonds were almost all cleaved. As

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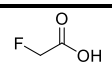
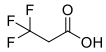
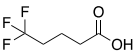
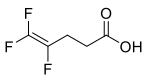
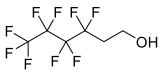
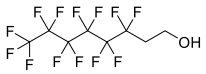
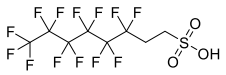
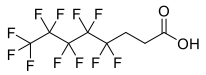
Table 1. Aerobic Microbial Defluorination of Polyfluorinated Carboxylic Acids and Precursors

FCA	Max. defluorination degree	Parent compound removal	Proposed defluorination pathway
 monofluoroacetate	100%	100%[21]	Hydrolytic defluorination
 2-fluoropropionic acid (**C3b**)	21%	100%[a]	Hydrolytic defluorination
 3,3,3-trifluoropropionic acid (**C3a**)	85%	100%[a]	HF elimination and Simultaneous cleavage of two sp^3 C−F bonds
 5,5,5-trifluoropentanoic acid (**C5a**)	37%[a] 47%[24]	100%[a] 6.3%[24]	Beta-oxidation→HF elimination and Simultaneous cleavage of two sp^3 C−F bonds[a]
 4,5,5-trifluoropent-4-enoic acid (**C5b**)	71%	30%[a]	Cleavage of the two sp^2 C−F bonds at the last carbon
 4:2 fluorotelomer alcohol	37%	74-91%[32, 33]	HF elimination
 6:2 fluorotelomer alcohol	16%	84-100%[33-40]	HF elimination
 8:2 fluorotelomer alcohol	12%	35-100%[16, 26, 41-46]	HF elimination
 6:2 fluorotelomer sulfonate	9%	7-100%[14, 23, 47, 48]	Desulfonation + HF elimination
 5:3 polyfluorinated carboxylic acid	N.A.	22%[18]	"One-carbon" removal pathway (alpha oxidation→HF elimination→reductive defluorination)

[a]This study. N.A.: not available.

the fluoride formation and **C3a** decay showed an approximately 3:1 molar ratio (Figure 1B) and the defluorination ceased upon **C3a** depletion, the cleavage of the three C−F bonds likely occurred simultaneously or very rapidly stepwise. A defluorination pathway was proposed in Figure 2A. After the activation of **C3a** (reaction ①), an HF elimination (reaction ②) occurred at the α-carbon, similar to the first step proposed for the 6:2 and 8:2 fluorotelomer carboxylic acids (FTCAs).[16,26] Then, hydration (reaction ③) occurred at the C═C bond, forming a difluoroalcohol, which was unstable[27] and quickly defluorinated into malonyl-CoA via spontaneous HF elimination (reaction ④) followed by hydrolysis (reaction ⑤). No transformation products were detected in the culture suspension or the cells, probably due to quick uptake, defluorination, and utilization of the formed small fatty acids by the cells or due to the small size and volatile property of the products that cannot be detected by the LC-HRMS.

The defluorination degree of the unsaturated structure (**C5b**) and the detection of the β-oxidation intermediate (3-hydroxyl acid) (Figures S6 and S7) support the proposed pathway of **C3a**. **C5b** could first undergo β-oxidation, forming a two-carbon-shortened structure with unsaturated α- and β-carbons (Figure 2B). It was then subject to a similar hydration reaction as reaction ③ in Figure 2A, followed by spontaneous cleavage of two C−F bonds at the end carbon, ending up with monofluoromalonyl-CoA (Figure 2B). A defluorination degree of ∼70% was observed for **C5b** (Figure 1A and D), consistent with the proposed pathway where two out of the three C−F bonds are cleaved. The incomplete transformation of **C5b** suggests that monofluoromalonyl-CoA could be toxic to cells and cause a halt of substrate uptake and turnover,[28] similar to the toxic fluoroacetate/fluoroacetyl-CoA.[29]

Trifluoropentanoic acid (**C5a**) was removed completely with some fluoride formation within 3 h. Then, the defluorination continued to a significant level (Figure 1C), indicating that it occurred to the primary transformation product of **C5a**, which could be 3,3,3-trifluoropropionic acid (**C3a**) via β-oxidation (Figure 2C) given the detection of 3-hydroxyl acid (Figures S6 and S7). However, the defluorination degree of **C5a** was only 37%, instead of nearly 100% for **C3a**. The reason could be a partial transformation of **C5a** via β-oxidation, and the rest was transformed via unclear nondefluorinating pathways. **C5a** could undergo α-oxidation similar to that previously reported, forming **C4a** that cannot be defluorinated.[18] However, no intermediates of α-oxidation of **C5a** or the product **C4a** were detected.

As a 2-haloacid, 2-fluoropropionic acid (**C3b**) is like monofluoroacetate and may also undergo hydrolytic defluorination (forming lactate), which can be catalyzed by 2-haloacid

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Environ. Sci. Technol. Lett. 2021, 8, 668−674

dehalogenases in aerobic bacteria.[22,30,31] **C3b** was completely transformed but only showed ∼20% defluorination after 72 h (Figure 1A). It indicates that 80% of **C3b** underwent nondefluorinating transformation pathways, which remain elusive as no plausible transformation products were identified. **C3b** could undergo decarboxylation, forming the volatile fluorinated alkane, which cannot be detected by LC-MS. Decarboxylation without defluorination could also occur to **C4b** and **c** that were biotransformed but not defluorinated, as well as **C3a**, which exhibited less than 100% defluorination.

Thus far, tremendous efforts have been invested in understanding the environmental fate and transport of FCAs using microcosms and microbial isolates.[16,33,34,36−39,42−51] In Table 1, we summarized the aerobic defluorination reported in the literature and this study for C_2−C_{10} FCAs and the alcohol precursors oxidizable to carboxylic acids. In the table, all defluorinated structures share a common feature: a functional group subject to enzymatic defluorination or nondefluorinating reactions that form unstable intermediates with fluoroalcohol moieties causing spontaneous C−F cleavage. Such functional groups include (i) C−H bonds at the α-position and (ii) sp^2 C−F bonds at the β-position. The n:2 fluorotelomer alcohols (FTOHs) and carboxylic acids (FTCAs) have α-C−H bonds. Their initial defluorination steps (n = 4, 6, 8) (Figure S8)[32,35] were similar to those proposed for **C3a** (1:2 FTCA) (Figure 2A). After the cleavage of two C−F bonds, n:2 FTCAs ($n \geq 2$) are turned into the two-carbon shorter perfluorinated acids, which are resistant to microbial oxidation. The reported maximum aerobic defluorination degrees for 6:2 (16%, 2 out of 13 F) and 8:2 (12%, 2 out of 17 F) FTOH/FTCA (Table 1) agree with the two C−F bond cleavage pathways. It also implies that defluorination via the other deeper defluorination pathways, such as forming three-carbon shorter perfluorinated acid and the "one-carbon removal" pathway,[18,40] were minor (Figure S8). Defluorination via the minor pathways could increase for shorter chain structures, as 4:2 FTOH had a 37% aerobic defluorination degree (3 out of 9 F), higher than that for two F removal (22%).[32] Besides the microbially attackable C−H bonds at the α-position, unsaturated α- and β-carbons tend to be subject to enzymatic hydration, which leads to spontaneous cleavage of the β-C−F bond(s) from the formed fluoroalcohol moiety.

Defluorination of C3a by Activated Sludge Was via Cometabolism. A cometabolic process is referred to as the degradation of nongrowth substrates with the obligate presence of a growth substrate.[52] We demonstrated that the nearly complete defluorination of **C3a** was cometabolic using biodefluorination experiments with **C3a** as the sole external substrate and with a growth substrate. When providing **C3a** (2 mM) as the sole external substrate in the fresh activated sludge, only 10% **C3a** was removed with ∼0.3 mM fluoride released after 72 h (Figure S9). It suggests that **C3a** was not able to sustain metabolic activities and support cell growth as the sole energy and carbon source. Since the first three steps of the **C3a** defluorination pathway (Figure 2A) were enzyme mediated, without growth substrates to conserve energy and synthesize new enzymes, the activities of the existing enzymes would decrease over time, rendering incomplete defluorination (50%). Also, the high concentration of **C3a** could be toxic and inhibit enzyme activities.

We further investigated the defluorination of **C3a** in 2% (v/v) sludge subcultures with and without a growth substrate. With **C3a** (50 μM) as the sole substrate, no defluorination or transformation of **C3a** was observed, whereas both propionate and glucose induced **C3a** defluorination (Figure S10), indicating cometabolism. Propionate led to a higher fluoride formation (41 vs 28 μM for glucose) (Figure S10), suggesting it is a better growth substrate to induce the propionate-utilizing enzymes, which seemed to cometabolize the structurally similar **C3a**. However, the defluorination degree was less than 30% after 18 days, which was much lower than that in the original activated sludge community (>80% after 3 days). It could be due to the reduced initial biomass, and the added growth substrate did not activate and maintain the cometabolic defluorination enzymes at a similar level as in the original activated sludge community. Cometabolic defluorination of FTOHs (n = 4, 6, 8) was also reported in *Pseudomonas* strains supplied with alkanes as the growth substrate.[32]

Environmental Implications. This study expands our fundamental knowledge of aerobic microbial defluorination of short-chain FCAs by activated sludge communities. The first implication of our findings is to the environmental fate of PFAS; the microbial aerobic defluorination, if any, is only to a limited degree for many PFAS structures. Only C−F bonds in specific structures are vulnerable to microbial cleavage, for example, β-C−F bonds with α-C−H bond(s) in carboxylic acids (or alcohols). To date, the reported aerobic defluorination of polyfluorinated structures was via either enzymatic HF elimination likely by acyl-CoA dehydrogenases[41] or spontaneous defluorination of unstable fluorinated intermediates, which are typically formed from enzymatic reactions at other functional moieties than C−F bonds.[16,17,26,41] Unless novel biocatalysts capable of cleaving C−F bonds at other positions could be discovered, aerobic microbial transformation of PFAS by activated sludge would end up with the accumulation of more persistent products from partial defluorination of the weak C−F bonds. Extensive screening of PFAS structures and biocatalysts is needed. The understanding of microbially susceptible C−F bonds can help predict the environmental fate of PFAS structures, thus guiding environmental risk assessment and regulations.

The second implication is to the treatment strategies of PFAS; although it may not be a stand-alone approach, microbial treatment could be integrated with physiochemical treatment for cost-effective performance. Perfluorinated structures can be defluorinated via advanced reduction by UV-generated hydrated electrons.[11] However, the unintended H/F exchange pathway forms more recalcitrant polyfluorinated byproducts, rendering incomplete defluorination.[11] Thus, microbial defluorination may be an economical post-treatment step to enhance the overall defluorination. **C3a** has been reported as the major byproduct of PFPrA after the advanced reduction treatment by a UV reactor.[12] We employed activated sludge to treat the PFPrA treatment effluent. Over 80% of organofluorine byproducts in the effluent were removed, mostly due to **C3a** defluorination (Figure S11). It achieved an additional 10%−15% defluorination (80%−85% defluorination combined). This result provides initial proof for the cost-effective chemical−biological PFAS treatment train system. Various polyfluorinated byproducts may be formed from incomplete chemical destruction of PFAS, many of which were not structurally elucidated.[11,12,53,54] Further demonstrations of the integrated chemical−biological treatment is needed via systematic investigation of the structures and biodefluorination efficacy of chemical treatment byproducts.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.1c00511.

Supplementary methods, detailed information on FCAs, DO levels, cross-validation of fluoride ISE measurement using IC, LC-HRMS/MS results of parent compounds and transformation products, defluorination with **C3a** as the sole substrate and with a cosubstrate, and defluorination of PFPrA chemical treatment effluent by the activated sludge community (PDF)

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Notes

The authors declare no competing financial interest.

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