Environmental Science & Technology

pubs.acs.org/est

Critical Review

Perfluoroalkane Sulfonamides and Derivatives, a Different Class of PFAS: Sorption and Microbial Biotransformation Insights

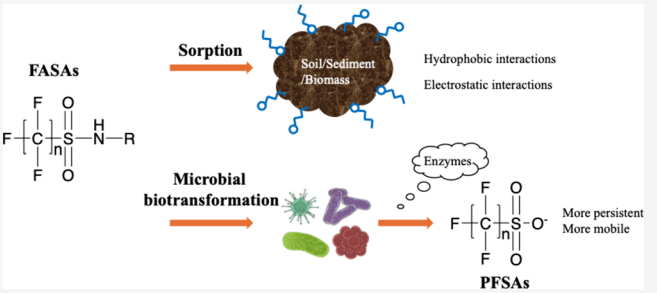
Donghui Ma and Christopher I. Olivares*

Cite This: *Environ. Sci. Technol.* 2025, 59, 10734−10749

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Perfluoroalkane sulfonamides and their derivatives (FASAs), an emerging subclass of per- and polyfluoroalkyl substances (PFAS), have attracted increasing attention due to their widespread applications, environmental persistence, and potential biological toxicity. Unlike perfluoroalkyl acids (PFAAs), FASAs can be transformed by microorganisms in the environment, producing fluorinated intermediates that eventually form stable PFAAs. A key difference of FASAs is that their pK_as enable them to exist as neutral species or zwitterions, unlike all other PFAS subclasses, which are all anions. Sorption processes regulate the bioavailability of FASAs to microorganisms for transformation, driving the environmental transport and fate of FASAs. In this critical review, we provide a comprehensive overview of the classification, properties, and environmental fate of FASAs, with a focus on sorption and microbial transformation. We discuss recent advancements in understanding the sorption of FASAs onto soil, sediment, and microbial biomass, including key sorption descriptors and influencing factors. Additionally, we examine the microbial biotransformation of FASAs, detailing transformation pathways, key intermediates, transformation kinetics, and enzymes involved. Finally, we identify critical research gaps and propose future directions to advance the study of the sorption and biotransformation of FASAs in environmental systems. Mechanistic understanding of these processes is crucial for managing sites impacted with FASAs.



KEYWORDS: *Perfluoroalkane sulfonamides, sorption, microbial biotransformation, PFAS, biotransformation enzymes*

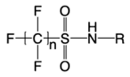
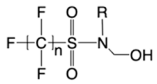
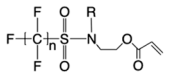
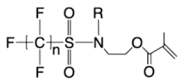
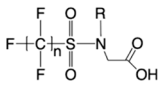
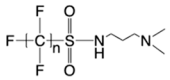
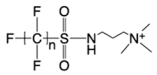
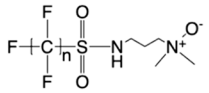
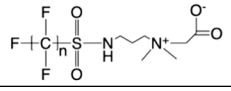
1. INTRODUCTION

Perfluoroalkane sulfonamides and their derivatives (FASAs) are an emerging class of perfluoroalkyl and polyfluoroalkyl substances (PFAS). FASAs have a perfluoroalkyl chain attached to a sulfonamide group, with possible additional N-substitutions (Table 1). A detailed list of FASAs, including their acronyms, CAS numbers, and chemical structures, is provided in Table S1 of the Supporting Information. FASAs have been used alongside other PFAS in various industrial and consumer products, such as aqueous film-forming foams (AFFF),[1,2] fabric protectors,[3] and firefighter turnout gear textiles.[4] Notably, FASAs continue to be used today, with some serving as replacements for legacy PFAS. Some short-chain FASAs, including perfluorobutane sulfonamide (FBSA; subclass 1 in Table 1) and perfluorobutane sulfonamide ethanol (FBSE; subclass 2), have recently substituted perfluoroalkyl acids (PFAAs) in semiconductor manufacture.[5,6] *N*-Ethyl perfluorooctane sulfonamide (EtFOSA, subclass 1) has been extensively used as an active ingredient in the pesticide sulfluramid.[7] Glüge et al.[8] noted that three FASAs (potassium *N*-ethyl perfluorooctane sulfonamidoacetate (subclass 5), perfluorooctane sulfonamidoalkyl ammonium iodide (subclass 7), and perfluorooctane sulfonamidoalkyl ammonium chloride (subclass 7)) are among the PFAS with high usage frequency, because they have more than ten assigned applications in commerce. With the recent availability of standards and advancements in suspect screening techniques, the detection frequency of FASAs in environmental and biological samples has increased.[2,9−14] Concerningly, FASAs exhibit a potential biological toxicity. FASAs were the only type of PFAS that influenced developmental, morphological, and behavioral outcomes in zebrafish embryos.[15,16] FOSA, MeFOSA, and FHxSA even showed higher toxicity than perfluorooctanesulfonate (PFOS).[16] The sulfonamide group is associated with antimicrobial properties, a characteristic that has been exploited in the development of many nonfluorinated antibacterial agents.[17] Unlike PFAAs, which are anionic, FASAs can exist in protonated forms at environmentally relevant pH levels.[18] This unique property and varying nonfluorinated moieties affect their environmental transport and fate, making them distinct from the majority of PFAS.

Received: January 19, 2025
Revised: May 8, 2025
Accepted: May 9, 2025
Published: May 26, 2025

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

Table 1. Subclass Structures for Nine FASAs and Their Main Uses[8,19,a]

Subclass	Chemical structure	Chemical name	Use
The blue 'A' represents alkyl length. For n = 4, 6, 8, A = B (butane), Hx (hexane), O (octane)			
1		where R=H, Perfluoroalkyl sulfonamides (FASA)	Major raw material for surfactant and surface protection products
		R=alkyl (methyl, ethyl), N-alkyl FASA (MeFASA, EtFASA)	
2		where R=H, Perfluoroalkane sulfonamidoethanols (FASE)	Major raw material for surfactant and surface protection products
		R=alkyl (methyl, ethyl), N-alkyl FASE (MeFASE, EtFASE)	
3		Where R=alkyl (methyl, ethyl), N-Alkyl perfluoroalkane sulfonamidoethyl acrylates (FASAC)	Major raw material for surfactant and surface protection products
4		Where R=alkyl (methyl, ethyl), N-Alkyl perfluoroalkane sulfonamidoethyl methacrylates (FASMAC)	Major raw material for surfactant and surface protection products
5		where R=H, Perfluoroalkane sulfonamidoacetic acids (FASAA)	Intermediate environmental transformation product
		Where R=alkyl (methyl, ethyl), N-alkyl FASAA (MeFASAA, EtFASAA)	
6		N-dimethyl ammonio propyl Perfluoroalkane sulfonamide (AmPr-FASA), also refered to as PFASAm	Functioning surfactants in AFFF-formulations
7		N-trimethyl ammonio propyl Perfluoroalkane sulfonamide (TAmPr-FASA), also refered to as PFASAmS	Functioning surfactants in AFFF-formulations
8		Perfluoroalkane sulfonamido amine oxides (PFASNO)	Functioning surfactants in AFFF-formulations
9		Perfluoroalkane sulfonamido betaine (PFASB)	Functioning surfactants in AFFF-formulations

[a]This is not an exhaustive list but includes reported FASAs with commercial standards.

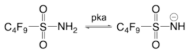
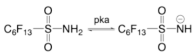
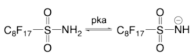
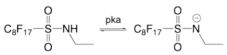
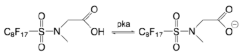
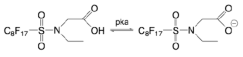
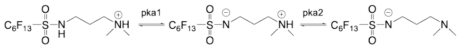
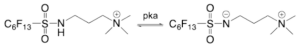
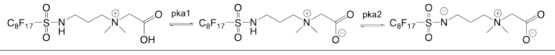
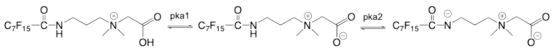
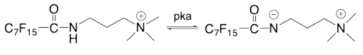
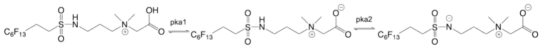
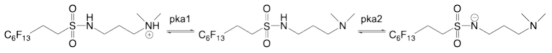
Sorption and microbial transformation affect the transport and fate of FASAs in the environment. Previous studies demonstrated that PFAA sorption to soil is controlled by hydrophobic and electrostatic interactions. PFAA adsorption increases with sediment organic matter content, solution ionic strength, and perfluoroalkyl chain length.[20] Perfluoroalkanesulfonates (PFSAs) show higher adsorption than perfluoroalkyl carboxylic acids (PFCAs) with comparable chain lengths.[21,22] Due to the different electrostatic charge (zwitterionic and neutral) compared to PFAAs (anionic) and diverse terminal functional groups of FASAs, their sorption mechanisms are expected to be more complex. To date, the sorption of FASAs in environmental media has been intermittently reported along with PFAAs data, and few dedicated studies on FASAs sorption exist. Beyond soils and aquifer solids, the sorption onto microbial biomass and biofilm can also influence the retention and transport of FASAs in environmental matrices.[23] PFAS sorption onto biomass has just started to be evaluated.[24−26]

PFAS are often considered biologically recalcitrant, although this primarily applies to PFAAs.[27] While some studies have reported PFAAs loss in various microbial cultures, the mechanisms continue to be debated and PFAAs remain biologically recalcitrant in most environmental settings.[28−32] In contrast, FASAs have been shown to undergo microbial transformation in natural environments, leading to the formation of terminal products—PFAAs, primarily PFSAs.[33−37] As a result, FASAs are designated as PFAS precursors. Unlike the more widely studied fluorotelomers (FTs), microbial transformation of FASAs yields PFSAs of the same perfluoroalkyl chain length, whereas fluorotelomers typically generate n to $n - 2$ PFCAs.[36,38] FASAs have been reported to have greater recalcitrance compared to fluorotelomers,[36] but over the long term the transformation products formed appear to be more persistent and mobile.

Therefore, a comprehensive review of the sorption and microbial transformation of FASAs is crucial for understanding their transport and fate in the environment as well as for providing a theoretical foundation for the management of contaminated sites. Although previous reviews on the environmental fate of PFAS have included the microbial transformation pathways of some FASAs,[33,35−37] they have not focused on the role of sorption processes, evaluated their microbial transformation kinetics, or provided detailed explanations of the underlying microbial transformation mechanisms. Therefore, this review aims to (1) examine the literature on the sorption of FASAs onto soil and microorganisms, summarizing sorption descriptors and influencing factors, (2) review the microbial transformation of FASAs in environmental media, including transformation pathways, key intermediates, final products, and transformation kinetics, (3) identify and discuss microbial enzymes involved in the

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

Table 2. Reported log K_d and pK_a Values of FASAs and Some Reference PFASs[a]

Compounds	Speciation	pKa values	log Kd (mL/g)	pH conditions	References
FASAs					
FBSA		6.27, 5.98[E]	-0.5	3.4-8.3	Nguyen et al., 2020
FHxSA		6.25	0.2	3.4-8.3	Nguyen et al., 2020
FOSA		6.2-6.52	1.2	3.4-8.3	Nguyen et al., 2020
			1.79	3.2-8.6	Campos-Pereira et al., 2023
EtFOSA*		9.0, 9.5[E]	3.21	2.9-6.1	Campos-Pereira et al., 2022
MeFOSAA		2.92	1.46	5.7-7.0	Higgins et al., 2006
EtFOSAA		3.9	1.29	5.7-7.0	Higgins et al., 2006
AmPr-FHxSA		(pka1)3.57; (pka2)9.21	1.1	3.4-8.3	Nguyen et al., 2020
TAmPr-FHxSA		3.28	1.3	3.4-8.3	Nguyen et al., 2020
PFOSB		(pka1)2.26; (pka2)6.78	0.94-1.08	5.2-7.6	Mejia-Avendaño et al., 2020
Reference PFAS					
PFOAB		(pka1)2.25; (pka2)7.79	0.48-0.81	5.2-7.6	Mejia-Avendaño et al., 2020
PFOAAmS		7.71	1.51-1.69	5.2-7.6	Mejia-Avendaño et al., 2020
6:2 FTAB		(pka1)2.26-2.81; (pka2)11.12	0.67-0.91	5.2-7.6	Mejia-Avendaño et al., 2020
6:2 FtSaAm		(pka1)9.2; (pka2)10.7	0.25	3.4-8.3	Nguyen et al., 2020
			2.81	5.2	Barzen-Hanson et al., 2017

[a]All pK_a values in this table were estimated by modeling,[39,42,43,47] except those marked with a superscript "E", which indicate experimentally determined values by 3M company.[48] All log K_d values were experimentally determined,[39−41,49] except for PFOSB, PFOAB, PFOAAmS, and 6:2 FTAB, which were calculated based on the Freundlich model due to the original experimentally determined values not being reported.[42] *Note: Organic carbon partition coefficient (K_{oc}) is provided for EtFOSA as no reported K_d values were found.

biotransformation of FASAs, and (4) highlight key knowledge gaps and propose opportunities for further research.

2. SORPTION OF FASAS

2.1. pK_a of FASAs. FASAs are different from other PFAS because the NH_2 in the sulfonamide group can exist in protonated (neutral) or deprotonated forms (negatively charged) at environmentally relevant pHs. Additionally, some FASAs contain N-substitutions with charged head groups, such as carboxyl, trimethylammonium, and quaternary ammonium. This means that FASAs can be present as anions, cations, or zwitterions or neutral species under different environmental conditions. As such, the pH-dependent protonation and deprotonation processes of FASAs need to be considered to evaluate the sorption. In Table 2, we list the reported experimental and calculated pK_a values of FASAs and several reference PFAS. Most of these data were estimated based on various models, including SPARC, Chemicalize, and ACD/Laboratories.[39,42,43,47] Only the pK_a values of FHxSA and EtFOSA were obtained experimentally by 3M Company.[48] The pK_a values of the sulfonamides range from 3.28 to 11.12 (Table 2). Based on computational estimates, Rayne et al.[18] indicated that alkylation of the parent perfluoroalkyl sulfonamides increases the pK_a compared to N-unsubstituted FASAs: *N*-methyl (2−3 log increase), N-ethyl/ethanol (2−3 log increase), and N-acetate (1−2 log increase). The degree and proximity of branching of the perfluoroalkyl chain also increases the sulfonamide pK_a, up to a 3−4 log difference between isomers. The length of the perfluoroalkyl does not appear to have a significant effect on sulfonamide pK_a values. It is important to note that pK_a predictions have been based on nonfluorinated aromatic and alkyl-substituted sulfonamide experimental data.[18] Thus, these predicted sulfonamide pK_a values still need to be validated experimentally.

2.2. Sorption onto Soils and Sediments. PFAS sorption to soils drives their transport and fate into the surface and groundwater. Theoretically, only PFAS not adsorbed by soil can infiltrate groundwater and be bioavailable to (micro)-organisms. The soil-water partition coefficient (K_d) is extensively employed to quantify the sorption of PFAS and other organic contaminants in soils and is defined as the ratio of the PFAS soil concentration with respect to the aqueous concentration. K_d is a soil-specific parameter influenced by the organic carbon content (OC), clay composition, cation exchange capacity (CEC), and anion exchange capacity (AEC), among other soil properties. The variable electrostatic charge and diverse head functional groups of FASAs, make their adsorption mechanisms more complex than anionic

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

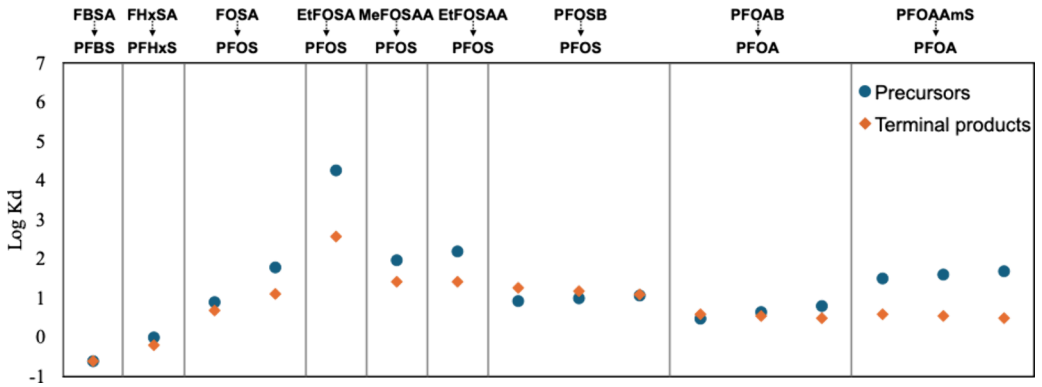


Figure 1. Comparison of log K_d values between FASAs (blue circles) and their potential terminal transformation products (yellow diamonds).[39−42,49] The two sets of data for FOSA are from different sources.[39,40] The three sets of data for PFOSB, PFOAB, and PFOAAmS are three calculated log K_d values at different liquid-phase concentrations based on the Freundlich model.[42] Aside from the data for PFOSB, PFOAB, and PFOAAmS, all other data were obtained experimentally.[39−41,49] The data for EtFOSA and matched PFOS represents log K_{oc} values, as log K_d values were not reported in the original literature.[49]

PFSAs. We compiled log K_d values of various FASAs along with reference PFAS (Table 2), including the amide analogs of PFOSB and PFOSAmS-perfluorooctane amido betaine (PFOAB) and *N*-trimethyl ammonio propyl perfluorooctane amido (PFOAAmS), as well as the fluorotelomer analog of PFOSB, 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), and the fluorotelomer analog of AmPr-FHxSA, 6:2 fluorotelomer sulfonamido amine (6:2 FtSaAm). The soil characteristics used in the referenced studies, including soil texture, CEC (cmol/kg), and anion exchange capacity (cmol/kg), are summarized in Table S2 of the Supporting Information. To contextualize the change in sorption potential because of FASA transformation, we compared the log K_d values of FASAs with those of their potential terminal transformation products, PFAAs (Figure 1). The log K_d values of FASAs and their paired PFAAs are derived from the same study.[39−42,49] Overall, most FASAs exhibit K_d values higher than those of their end products. This suggests that the microbial transformation of FASAs under natural conditions generates more mobile PFAS, likely leading to more widespread aqueous contamination.

Multiple studies have shown statistically significant positive correlation of OC values with the K_d values of FOSA,[39,40] FBSA,[39] and *N*-alkyl FASAAs (MeFOSAA, EtFOSAA).[41] This indicates that hydrophobic interactions play an important role in the sorption of anionic and neutral FASAs. In contrast, the cationic and zwitterionic FASAs have not shown significant correlation with K_d and OC values.[39,42,43] The K_d values of some cationic and zwitterionic FASAs (AmPr- and TAmPr-FHxSA) were dominantly and positively impacted by exchangeable sodium percentage (ESP) and CEC,[39,42] in agreement with zwitterionic fluorotelomer studies.[43,44] CEC reflects the capacity of soil to hold onto cations resulting from the negatively charged organic matter and clay particles through electrostatic interactions. The higher the CEC values, the more negatively charged the organic matter and clay sites are for the adsorption of cationic FASAs. In addition, the increase in the CEC value may extend the basal plane spacing of some clay minerals, providing more volume for sorption.[45] Although few studies have reported significant correlations between the combined content of silt and clay in soil and the K_d values of certain PFAS, including FOSA (positively correlated) and 6:2 FTAB (negatively correlated), their predictive strength was weak to moderate (R^2 = 0.52−0.57).[39,40]

pH not only affects the charge properties of the soil surface but also affects the charge state of FASAs, affecting the adsorption behavior of FASAs. For the FASAs and derivatives reviewed, the K_d values generally decrease with the increase in solution pH, but these effects depend on whether their pK_as were in the evaluated pH range (Table 2). MeFOSAA and EtFOSAA (pK_a range 2.92−3.9) remain in anionic form within the tested pH range (5.7−7).[41] Then, the pH-induced change in K_d values would instead impact the soil surface charge and/or hydrophobicity. At low pH, soil OC is more protonated, which could decrease repulsion of anionic FASA moieties.[46] As pH increases, soil OC and clay minerals become progressively more negatively charged, causing electrostatic repulsion of anionic FASAs and reducing sorption.[46] For FASAs with pK_a > 6, the increase in pH has a greater impact on reducing adsorption, as higher pH leads to deprotonation of FASAs, enhancing electrostatic repulsion with the soil.[39,43] Nguyen et al.[39] observed that the most drastic changes in K_d values of FBSA, FHxSA, and FOSA were apparent when the solution pH increased from approximately 5 to 7. Within this range, these FASAs may be rapidly ionized from neutral molecules into anions. Similarly, a drastic reduction in K_d for PFOSB was observed between pH 5.4 and 7.6,[42] which corresponds to its sulfonamide pK_a. In addition, K_d values of zwitterionic AmPr-FHxSA (pK_{a1} 3.57, pK_{a2} 9.21) and TAmPr-FHxSA (pK_a 3.28) showed high sensitivity to changes in pH between ∼7 and 8.[39] However, their predicted pK_a values did not indicate deprotonation of the sulfonamides between pH ∼7 and 8, which may suggest inaccurate pK_a predictions. PFOAB, PFOAAmS, and 6:2 FTAB did not exhibit strong pH-dependent adsorption within the studied pH range (4−7),[42] probably because their pK_as fall outside environmentally relevant pHs.

The perfluorocarbon chain, molecular weight, functional groups, and charge exhibit important impact on the sorption behavior of FASAs. The K_d values of FBSA, FHxSA, and FOSA increase sequentially, suggesting increased hydrophobic interactions with the increasing perfluoroalkyl chain.[39] PFOSB showed stronger sorption than PFOAB,[42] which is consistent with stronger PFSA sorption compared to PFCAs. This could be due to the presence of one additional carbon atom and larger molar volume of the sulfone group in

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

sulfonamide compared to that of the carbonyl in amides. EtFOSA, an eight-carbon analog, was found to show stronger sorption in soil than FOSA,[49] which indicated the addition of an ethyl group to the $-SO_2-NH-$ headgroup appeared to have enhanced sorption. Relatively minor differences in sorption were observed between N-MeFOSAA and EtFOSAA;[41] the additional N-alkyl carbon had little impact on sorption. Additional sorption studies involving N-alkyl FASAAs (i.e., *N*-butyl-FOSAA) and N-alkyl FASAs (i.e., MeFOSA) may contribute to an enhanced understanding of the impact of N-atom substituents on the sorption of these compounds via sulfonamide pK_a. Comparing FASAs with reference PFAS with identical fluorinated carbon chains, the K_d values were highest for cationic species, followed by zwitterionic species, and lowest for anionic species (AmPr- and TAmPr-FHxSA > 6:2 FTAB > FHxSA > PFHxA). This is in good agreement with findings in perfluoroalkyl amides (PFOAAmS > PFOAB)[42] and FTs (6:2 FtSaAm > 6:2 FTAB > 6:2 fluorotelomer sulfonate (6:2 FTS)),[43] which indicates the electrostatic interaction is an important mechanism in the adsorption process of all of these polyfluorinated compounds.

2.3. Sorption by Bacteria (Biosorption) of FASAs and Sulfonamide Antibiotics. The sorption of PFAS onto microbial biomass and biofilm can influence the retention and transport of PFAS in environmental matrices.[23] However, microbial adsorption of PFAS has just started to be evaluated.[24−26] Previous batch biosorption studies have evaluated sorption of PFAAs.[23,25,50−52] The molecular structure of PFAS, solution chemistry, and cell membrane structure can affect the magnitude of the PFAS sorption. Some research indicated that bacteria showed stronger adsorption with long-chain PFAS compared to short-chain PFAS,[52] and bacterial sorption was greater for PFOS than for perfluorooctanoic acid (PFOA),[25,52] which aligns with findings from PFAS sorption studies in soil.[39] The hydrophobic components in the cell membrane (e.g., phospholipids), along with the extracellular polymeric substances (EPS, composed of polysaccharides, proteins, and lipids)[53] produced by the cells, may provide hydrophobic and electrostatic PFAS binding sites.[26,54] Butzen et al. reported that PFOS sorption onto bacteria varied with pH, with greater sorption at pH ∼4 compared to pH 6.[25] As pH increases, binding sites (such as peptides) on the cell surface deprotonate and repel anionic PFAS. Bacteria have negative-bulk charges at neutral pHs—their isoelectric point (pI) ranges from pH 2−5—and Gram-positive bacteria have a wider pI range compared to Gram-negative.[55,56] Based on differences in cell membrane composition, these two groups are hypothesized to exhibit different adsorption capacities, but studies have yielded contradictory results to date. A study suggested that Gram-negative bacteria show a stronger PFAS sorption capacity because of higher lipid content stemming from the double membrane bilayer.[52] However, another study found greater sorption of PFAS by Gram-positive bacteria.[25] With an outward-facing and thicker peptidoglycan, more peptide sorption sites have been hypothesized[57] to increase PFOS sorption in Gram-positive bacteria. Lastly, Dai et al.[23] found no significant difference in PFAS sorption capacity between different Gram-stain bacteria. Bacteria can retain PFAS through sorption onto cell surfaces and uptake into the cell interior. Butzen et al.[25] suggested PFOS bacterial sorption was rapid and completely reversible, indicating that biosorption is likely a cell surface phenomenon within the test period (80 h). On the other hand, studies showed inactivated bacteria retained PFAS significantly less than active bacteria.[52,58] Presentato et al.[59] reported that two *Pseudomonas* sp. strains were able to accumulate PFHxS within the cells in a short period (∼15 days), indicating the incorporation of PFAS into the cells. Studies on animal cells have shown that passive diffusion and protein-facilitated transport are the primary mechanisms for PFAS uptake into cells.[60−63]

Certain nonfluorinated sulfonamide antibiotics, including sulfamethoxazole (SMX), sulfadimethoxine (SDM), and sulfamonomethoxine (SMM), are adsorbed onto wastewater activated sludge. At the experimental pH 6.8, the sorption affinity of sulfonamide antibiotics to activated sludge followed the order of SDM (pK_a 6.3) > SMM (pK_a 6.0) > SMX (pK_a 5.7), which is consistent with the order of pK_a values of the $-SO_2-NH-$ moiety.[64,65] In addition, Pi et al.[66] reported that the fluorescence intensity of certain hydrophobic amino acids (such as the aromatic amino acids tryptophan and tyrosine) in EPS significantly decreased after adsorbing sulfonamide antibiotics. Based on these observations, it is reasonable to hypothesize that both pK_a and hydrophobicity significantly influence the sorption behavior of FASAs, with EPS likely playing a critical role in this process.

EPS is known to decrease bacterial pI[55] and thus possibly increase sorption capacity for PFAS. PFAS sorbed can create a feedback loop for EPS production. For example, PFAAs have been shown to induce EPS-production in *Rhodococcus jostii* as a stress response mechanism.[67] So far, no studies have directly investigated the interactions between bacterial surfaces and EPS with FASAs. Ruyle et al.[24] reported large and rapid losses of 3 FASAs (AmPr-FHxSA, TAmPr-FHxSA, and FHxSA) from the aqueous phase in bioactive microcosms, indicating rapid sorption onto cells (<1 day). Faster biosorption of AmPr-FHxSA and TAmPr-FHxSA was reported compared to FHxSA. Considering the findings of biosorption literature on PFAAs and nonfluorinated sulfonamide antibiotics, we hypothesize that FASAs may exhibit more complex adsorption behavior due to their diverse head groups and charge properties, as well as pH gradients that drive microbial metabolism across cell membranes. Additionally, the sulfonamide nitrogen may act as an electron donor, forming hydrogen bonds with electron acceptor groups on the cell surface (such as amide, amine, or hydroxyl groups), thereby stabilizing the sorption process.[68] Elucidating biosorption mechanisms of sulfonamide PFAS is crucial to evaluate their bioavailability for microbial transformation.

3. MICROBIAL BIOTRANSFORMATION

The adsorption of FASAs onto solid-phase media hinders their microbial transformation. Additionally, the high surface activity of PFAS can promote self-aggregation and enrichment at the air−water interface, further reducing its bioavailability to microorganisms.[69] Slower microbial biotransformation kinetics have been reported for electrochemical fluorination-derived (ECF) PFAS compared to fluorotelomers because the alpha and beta nonfluorinated carbons with respect to the perfluoroalkyl chain can serve as oxidizable moieties.[36,37,66] Despite the slower kinetics, decades of application of FASAs to the environment can yield substantial transformation. Microbial transformation kinetics are crucial to predicting the long-term fate of these precursors. We examined the microbial transformation rates of FASAs by comparing their first-order half-lives ($t_{1/2}$, Table 3). Additionally, we summarized their

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

Table 3. Reported Microbial Biotransformation of FASAs and Their Test Conditions with Product Yields[a]

Compound	Incubation conditions	PFAS initial concentrations	Duration	$t_{1/2}$ (days)	Mass balance and transformation products (mol %)	References
EtFOSE	WWTP activated sludge, aerobic, 28 ± 2 °C	2.38 mg/L	35 d	2−3	Mass balance 100.6 ± 16.3%, EtFOSAA (34.9%), FOSAA (48.9%), FOSA (5%), PFOSI (3.5%), PFOS (7%), EtFOSA (0.1%)	Lange et al., 2000
EtFOSE	WWTP activated sludge, aerobic, 25 °C	1.5 ± 0.05 mg/L	96 h	3	EtFOSAA (23 ± 5.0%), PFOSI (5.3 ± 0.8%)	Boulanger et al., 2005
EtFOSE	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.71 ± 0.05	Mass balance 111%, EtFOSAA (66%), EtFOSA (1%), FOSAA (7%), FOSA (18%), PFOSI (1%), PFOS (7%)	Rhoads et al., 2008
EtFOSE	Marine sediments, aerobic, 25 °C	0.0625 mg/L	120 d	44	Mass balance 84%, EtFOSAA (31%), EtFOSA (1.7%), PFOS (0.44%), FOSAA (0.43%), FOSA (0.21%)	Benskin et al., 2013
EtFOSE	Marine sediments, aerobic, 4 °C	0.0625 mg/L	120 d	160	Mass balance 95%, EtFOSAA (39%), PFOS (12%), EtFOSA (6.4%), FOSAA (2.8%), FOSA (2.8%),	Benskin et al., 2013
EtFOSE	Acidic forest silt loam (pH = 5.5, OC 2.4%), aerobic, 22 ± 2 °C	3.7 μg/g	210d	26	Mass balance 97 ± 12%, EtFOSAA, FOSSA, FOSA, PFOS (1.06%)	Zhang et al., 2017
EtFOSE	Agricultural loam (pH = 7.8, OC 2.6%), aerobic, 22 ± 2 °C	3.7 μg/g	180d	31	Mass balance 102 ± 3%, EtFOSAA, FOSSA, FOSA, PFOS, PFOS (5.49%)	Zhang et al., 2017
EtFOSE	Anaerobic digester sludge, 20−26 °C (1010 mg/L)	1010 mg/L	108 d	1860	Mass balance 92%, EtFOSAA (1.7%), PFOSI (0.3%)	Lange et al., 2017
n-EtFOSE	Soil, aerobic, 22 °C	2.696 μg/g	105 d	9.6	Mass balance 60−83%, n-FOSAA (49%), n-FOSA (0.47%), n-FOSAA (3.6 %), n-FOSA (12%), and n-PFOS (7.9%)	Liu et al., 2019
br-EtFOSE	Soil, aerobic, 22 °C	2.696 μg/g	105 d	8.7	br-EtFOSAA,br-PFOS, br-FOSAA, br-FOSA	Liu et al., 2019
MeFBSE	Anaerobic digester sludge, 20−26 °C	976 mg/L	108 d	35.8	Mass balance 122% (92−122%), MeFBSAA (57%), PFBSI (40%)	Lange et al., 2017
EtFOSA	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.24	Mass balance 73%, FOSA (55%), FOSAA (2%), PFOSI (2%), PFOS (41%)	Rhoads et al., 2008
EtFOSA	Soil, aerobic	1.62 mg/L	182 d	13.9 ± 2.1	Mass balance 71%, FOSA (30.3%), FOSAA (34.2%), EtFOSA (2.21%), PFOS (4%)	Mejia-Avendaño et al., 2015
EtFOSA	Slurry from wetland, aerobic, 30 °C	0.47 μg/g	91 d	0.51	Mass balance 99.7−131.4%, FOSAA, FOSA, PFOS (85.1%)	Yin et al., 2018
EtFOSAA	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.025	Mass balance 62%, EtFOSA (1%), FOSAA (5%), FOSA (18%), PFOS (10%)	Rhoads et al., 2008
FOSAA	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.11 ± 0.04	Mass balance 72%, FOSA (38%), PFOSI (2%), PFOS (21%)	Rhoads et al., 2008
FOSA	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.02	Mass balance 83%, PFOSI (2%), PFOS (38%)	Rhoads et al., 2008
PFOSI	WWTP activated sludge, aerobic, 30 °C	0.1 mg/L	10 d	0.25 ± 0.02	Mass balance 86%, PFOS (78%)	Rhoads et al., 2008
PFOSAmS	Soil, aerobic, 22 °C	2.827 μg/g	180 d	no significant change	Mass balance 73.1%, PFOSAm (10%), FOSA (<0.005%), PFOS (0.3%)	Mejia-Avendaño et al., 2016
PFOSNO	Soil, aerobic	1.998 μg/g	90 d	15	Mass balance 15−16%, FOSAA, FOSA, PFOS(~2%)	Chen et al., 2020
PFOSAm	Soil, aerobic, 22 °C	2.0 μg/g	90 d	47.5	FOSAA (0.001%), FOSA (0.8%), PFOS (0.27%)	Liu et al., 2021
PFOSB	Soil, aerobic, 22 °C	1.8 μg/g	90 d	675	FOSAA (0.064%), FOSA (0.52%), PFOS (1.5%)	Liu et al., 2021
AmPr-FHxSA	Amended AFFF-impacted soil, 30 °C	0.097 mg/L	70 d	27.4	FHxSA (~40%), PFHxS (1−5.4%)	Cook et al., 2022
AmPr-FHxSA	Slurry,19 °C/29 °C, pH 6.0−7.2	6851 mg/L	45 d/ 60 d		FHxSA, PFHxS	Ruyle et al., 2023
AmPr-FHxSA	Slurry,19 °C/29 °C, pH 6.0−7.2	47501 mg/L	45 d/ 60 d		FHxSA, PFHxS	Ruyle et al., 2023
FHxSA	Slurry,19 °C/29 °C, pH 6.0−7.2	28729 mg/L	45 d/ 60 d		PFHxS	Ruyle et al., 2023

[a]Standard deviation for $t_{1/2}$ is reported whenever available.

transformation pathways (Figures 2 and 3) and major intermediates (Table 3) expected to persist in the environment at high levels. Finally, we reviewed the reported enzymes involved in microbial precursor transformation to hypothesize biochemical mechanisms of FASAs transformation.

3.1. Aerobic and Anaerobic Microbial Transformation of EtFOSE. EtFOSE is aerobically biotransformed into PFOS via intermediates, including EtFOSAA, EtFOSA, FOSAA, FOSA, and PFOSI, which all can be quantified by LCMS.[70−76] The aerobic microbial transformation half-life range of EtFOSE is <1 day to 160 days depending on the matrix and conditions. In general, the transformation rate of EtFOSE follows activated sludge > soil > marine sediments, which could be attributed to aerobic microbial density and activity in different media. Incubation conditions (e.g., temperature, pH) are expected to impact transformation rates and product yields. In a study of the transformation of EtFOSE in different soils, EtFOSE was transformed slightly faster in acidic soils, but PFOS yields in alkaline soils were four to five times higher than in acidic soils.[75] It was hypothesized

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

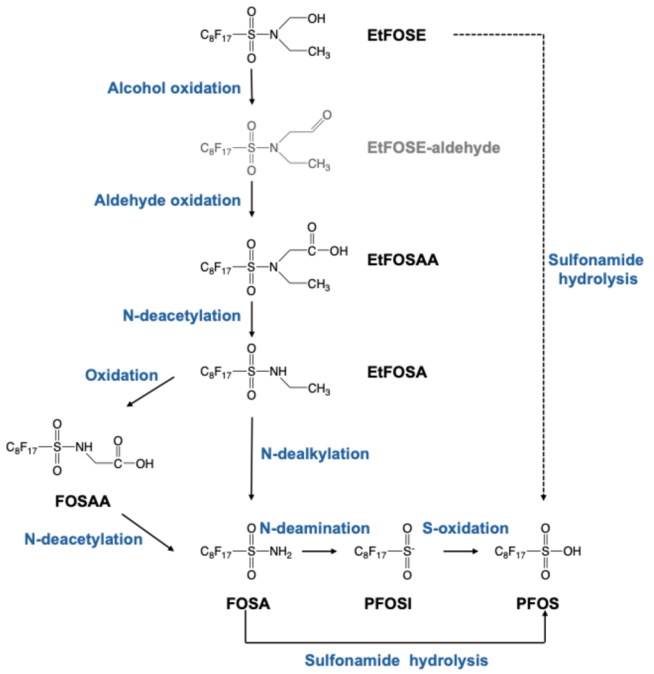


Figure 2. Microbial transformation pathways of EtFOSE.[70−76] Structures in gray are undetected, predicted intermediates. The solid line represents the primary pathways, and the dashed line represents the secondary pathways.

that varied soil properties resulted in differences in microbial communities and bioavailability of major intermediates, based on their pK_as. It has been demonstrated that the biotransformation half-lives of branched and linear EtFOSE show no significant difference.[76]

There are two main pathways for microbial transformation of EtFOSE (Figure 2): the primary pathway is a series of N-alkyl oxidations and N-dealkylations to yield FOSA, which can accumulate in the environment. The sulfonamide group in FOSA is hydrolyzed to yield PFOS, but with reported lower yields. Although a parallel transformation pathway leading to FOSE (N-deethylation) has been observed in fish,[77] FOSE has not been quantified in studies of microbial transformation due to unavailable analytical standards and its volatility. Zhang et al.[75] confirmed that the proposed pathway including FOSE did not fit the previous experimental data well. Previous studies have consistently demonstrated that EtFOSE can be transformed into EtFOSAA rapidly, accumulating and then remaining or slightly decreasing. EtFOSAA is considered the major intermediate, with yields ranging from 23% to 66%. Other persistent intermediates include FOSAA and FOSA, which are consistent with frequent reporting of coexistence of these substances with PFOS in soils, sludge, and landfill leachates.[78,79] However, PFOS accumulates relatively slowly during the incubation (maximum yield of 12% from EtFOSE after 120 d)[73] and even shows a continuously increasing trend at the end of the incubation duration, indicating the long-term accumulation of PFOS in the environment. In a microbial transformation study of EtFOSA by wetland microcosms,[80] an unexpectedly high yield of PFOS was reported at 85.1 mol % after 91 days of aerobic incubation. Meanwhile, the microbial community shifted to *Methylocaldum*, methanotrophs which are obligately aerobic and are able to utilize methane as their sole carbon and energy source.[81] Previous studies have shown that methanotrophs have a broad substrate profile and can cometabolize certain recalcitrant chemicals, like chlorinated ethenes.[82]

Some studies have reported microbial transformation behaviors of major intermediates of EtFOSE to identify the bottlenecks in PFOS yields.[72,74,80] FOSAA and FOSA are frequently identified as major intermediates from EtFOSAA and EtFOSA biotransformation.[72,74,80] Combined with the evidence that EtFOSAA is the main intermediate of EtFOSE,[70,73,75] it can be inferred that carboxylic acids are difficult to transform due to their oxidation state. Therefore, the removal of the N-acetic acid group and the hydrolysis of the sulfonamide are the major rate-limiting step.

Notably, Lange[83] reported the extremely slow transformation of EtFOSE with the half-life time of 1860 d in anaerobic digestion sludge. In contrast, MeFBSE exhibited a significant loss in anaerobic sludge with a half-life of 35.8 days and produced MeFBSAA (57%) and PFBSI (40%). This study suggested the potential for the anaerobic transformation of short-chain precursors and the formation of short-chain PFAAs. Currently, there is no evidence of abiotic transformation of FASAs in sterile environmental media.

3.2. Cationic and Zwitterionic N-alkylamine FASAs.

These cationic and zwitterionic N-alkylamine FASAs possess relatively large molecular weights and tertiary or quaternary amine moieties. Due to the diverse functional groups, they exhibit more complex microbial transformation compared to EtFOSE and EtFOSA. In studies of microbial transformations of cationic and zwitterionic *N*-alkyl amine-containing FASAs, large gaps in mass balance remain, with recoveries ranging from 15% to 73.1%, indicating unquantified and unidentified transformation intermediates. High-resolution mass spectrometry under full scan mode has been applied to identify anticipated biotransformation intermediates based on suspect lists,[24,36,84] as well as biodegradation prediction simulators (e.g., EnviPath, CATALOGIC).

We reviewed the microbial transformation pathways of cationic and zwitterionic ammonium-containing FASAs based on limited previous literature (Figure 3, Table 2). PFOSAmS, PFOSNO, and PFOSB can transform into PFOSAm at a relatively rapid rate through N-demethylation, N-oxide reduction, and N-deacetylation, which could be the major initial steps of these three precursors. Cook et al.[84] also detected perfluorohexane sulfonamidoalkyl amine oxide (PFOHxNO) among the transformation products of the six-carbon homologue (AmPr-FHxSA) of PFOSAm, which suggests the occurrence of N-oxidation of tertiary amines. PFOSAm could then undergo sequential N-demethylation and oxidation removal of ammonium, eventually forming polyfluoroalkyl sulfonamide aldehyde (PFOSAm-3); the aldehyde can also be directly generated from the parent compounds (PFOSAmS and PFOSNO) through the oxidative removal of the ammonium group. Subsequently, polyfluoroalkyl sulfonamide aldehyde undergoes sequential oxidation and hydrolysis in several steps to eventually form PFOS, which resembles the previously reported biotransformation process in the aerobic soil of EtFOSA.[74] FOSAA and FOSA are frequently detected as major transformation intermediates of these ammonium-containing FASAs, as well as key intermediates of EtFOSE and EtFOSA. This is consistent with the fact that FOSAA and FOSA (as well as shorter-chain homologues) are frequently detected and present at high levels in PFAS-contaminated sites.[5,85] The six-carbon homologue, AmPr-FHxSA was

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

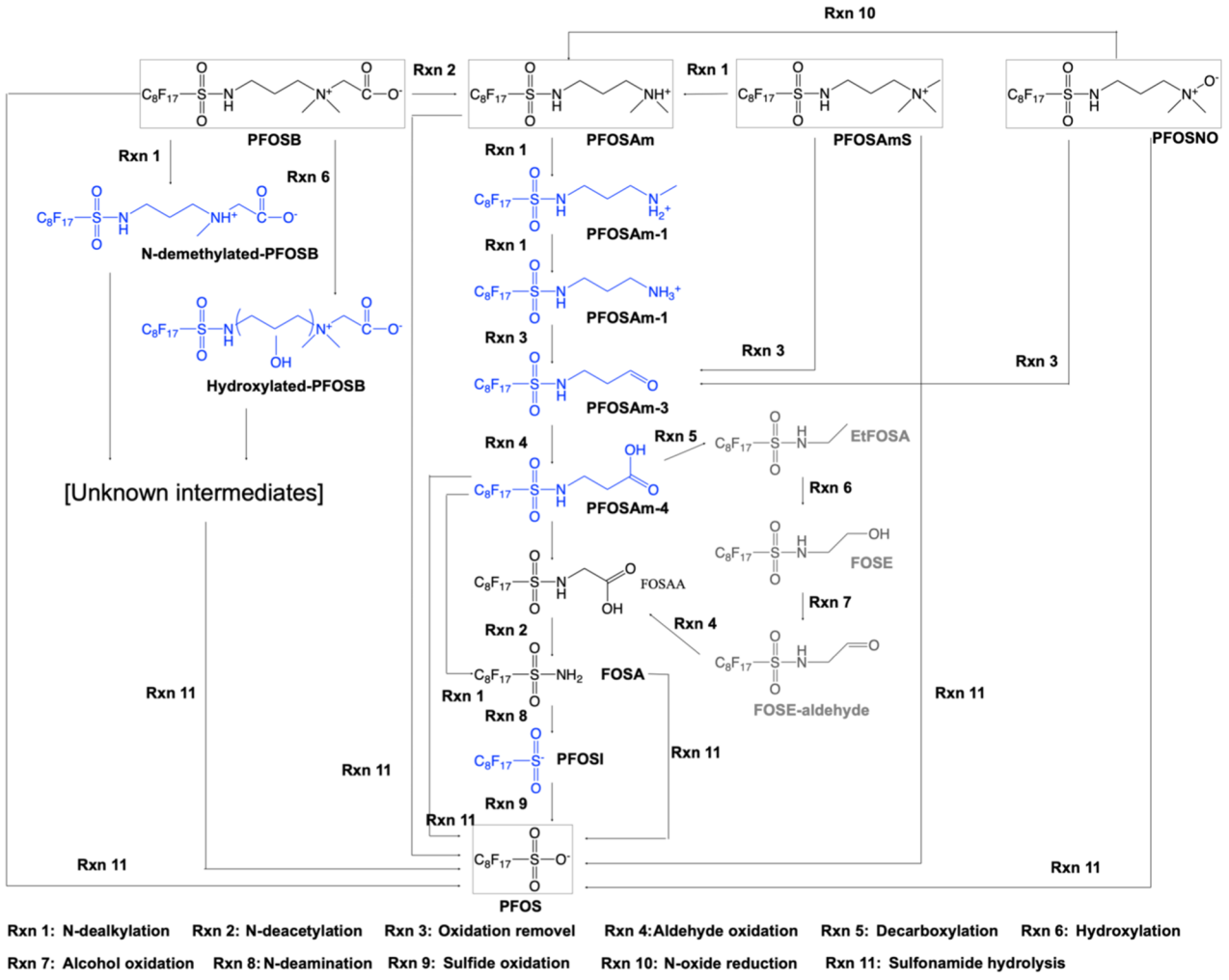


Figure 3. Microbial transformation pathways of cationic and zwitterionic amine-containing FASAs. Structures in blue are identified by suspect screening. Structures in gray are undetected, predicted intermediates.[24,84,86−88]

demonstrated to undergo similar microbial transformation processes as PFOSAm under aerobic conditions.[84]

Another pathway for PFOSAmS, PFOSNO, PFOSB, and PFOSAm is to generate PFOS through direct sulfonamide bond hydrolysis. Although previous literature only listed the direct hydrolysis pathways of PFOSAmS, PFOSNO, and PFOSAm, based on analogous reasoning, we included the direct hydrolysis of PFOSB in this review. Rayne et al.[89] indicated that abiotic hydrolysis at the S−N bond of N-unsubstituted FASAs appears unlikely under environmentally relevant conditions. However, N-ethanol and N-acetate moieties in perfluoroalkyl sulfonamido ethanols and acetates may self-attack the S−N bond and induce hydrolysis, leading to the formation of PFOS. In addition, as for transformation intermediates of PFOSB, Liu et al.[87] detected hydroxyl-substituted betaines and demethylated betaine, which suggest other two transformation pathways of PFOSB. However, the subsequent transformation processes of these hydroxylated or N-demethylated compounds are unknown.

Compared with the microbial transformation of neutral precursors (EtFOSE and EtFOSA) in aerobic soil ($t_{1/2}$: 9.6−31 d), these cationic and zwitterionic precursors ($t_{1/2}$: ~47.5 d) exhibit higher resistance to microbial transformation except for PFOSNO ($t_{1/2}$: 15 d). The presence of cationic groups significantly increases the electrostatic attraction to negatively charged soil particles. Both factors contribute to a decrease in microbial bioavailability.

The half-lives of FASAs are longer than those of their amide analogs with the same number of fluorinated carbons. Specifically, the observed $t_{1/2}$ values follow the trends PFOSB > PFOAB, PFOAAmS > PFOSAmS, *N*-dimethyl ammonio propyl perfluorooctane amido (PFOAAm) > PFOSAm and PFOSNO > perfluorooctane sulfonamido amine oxide (PFOANO). We hypothesize that the higher persistence of sulfonamides could be due to their stronger sorption to soil, resulting from a longer perfluoroalkyl chain and a bulkier sulfonyl group compared to corresponding amides, which in turn reduces their bioavailability for transformation. Additionally, the sulfonamide group is more resistant to hydrolytic cleavage than the amide group,[84] which could result in slow biotransformation kinetics of sulfonamides in microbial hydrolytic reactions.

The difference in microbial transformation rates between eight-carbon cationic and zwitterionic FASAs derived with varying N-alkyl substitutions is notable. When evaluating their stability in aerobic soil, their $t_{1/2}$ values exhibit a distinct pattern, quaternary amine ≈ propyl betaine ≫ tertiary amine > amine oxide,[87] which is consistent with the ranking in corresponding amides. Thus, terminal N-substitutions exert significant influence on the biotransformation rates of these

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

Table 4. Reported Enzymes Involved in Biotransformation and Defluorination of PFAS

Enzymes/proteins	Encoded gene	Function	PFAS substrate	Products	Source microorganisms	Research method	References
Alkanesulfonates-binding protein	SsuA	Alkanesulfonate assimilation/utilization	6:2 FTS	6:2 Fluorotelomer carboxylic acid (6:2 FTCA), 6:2 FTUA, 5:3 FTCA, PFHxA, PFPeA, fluoride ion	*Dietzia aurantiaca* J3	Identifying upregulated proteins in the presence of 6:2 FTS compared to sulfate through genome sequencing and annotation	Méndez et al., 2022
Alkanesulfonates ABC transporter ATP-binding protein	SsuB	Alkanesulfonate assimilation/utilization					
Alkanesulfonate monooxygenase	ssuD	Alkanesulfonate assimilation/utilization					
alkanesulfonate permease protein	SsuC	Alkanesulfonate assimilation/utilization					
nitrilotriacetate monooxygenase component B	ntaA-MoB	Amino acid catabolism					
alkane monooxygenase	RHA1_ro02534	Defluorination	6:2 FTOH, 6:2 FTS	6:2 FTCA, Perfluoroheptanoic acid (PFHpA), 6:2 FTUA, α-OH 5:3 FTCA, fluoride ion (from 6:2 FTS)	*Rhodococcus jostii* RHA1	Examining the expression levels of presumptive enzymes at different growing substrates; heterologous gene expression and in vitro assays	Yang et al., 2022
cytochrome P450	RHA1_ro00377	Defluorination	6:2 FTOH, 6:2 FTS				
haloacid dehalogenases	RHA1_ro00230	Defluorination	6:2 FTOH, 6:2 FTS				
alkanesulfonate monooxygenase	RHA1_ro01768	Desulfonation	6:2 FTS				
toluene dioxygenase		Transformation	6:2 FtTAoS	6:2 FTS, PFHxA, PFPeA, PFBA	microorganisms in AFFF-impacted soil	Examining the presumptive genes in the BTEX amended enrichments	Olivares et al., 2022
nitrilotriacetate monooxygenases	ntaA(ISGA 1218 and 1222)	Desulfonation	6:2 FTS	6:2 FTCA. 6:2 FTUA	*Gordonia* sp. strain NB4-1Y	Identifying differentially expressed proteins in the presence of 6:2 FTS compared to sulfate	Hamme et al., 2013
alkane hydroxylase	alkB	Transformation	6:2 PAPs	6:2 FTOH, 6:2 FTCA, 6:2 FTUA, PFHxA, fluoride ion	microorganisms in activated sludge	Examining the presumptive genes in the activated sludge enrichments	Lewis et al., 2016
haloacid dehalogenases	PZP66635.1, WP_011137954.1	Defluorination	PFOA	Fluoride ion	*Delftia acidovorans*	Heterologous gene expression	Harris et al., 2022
Fluc family F^- channel	crcB1 and crcB2	Functional fluoride exporter	PFMeUPA	Fluoride ion, $(CF_3)_2CFCF{=}CHCOO^-$, $(CF_3)_2CFCHFCH_2COO^-$, $(CF_3)_2CF(CHF)_2COO^-$	*Acetobacterium bakii*	Identifying upregulated genes in the presence of PFMeUPA compared to nonspiked control; Heterologous gene expression in *E. coli* Caffeate competitive inhibition of PFMeUPA defluorination; Molecular docking of caffeoyl-CoA and perfluorinated acyl-CoA with CarC	Yu et al., 2024
caffeoyl-CoA reductase	car operon (carABCDE)	Reductive defluorination					

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

precursors. The presence of a quaternary amine group significantly enhances the persistence of PFOSAmS and PFOSB. As a permanently cationic moiety, the quaternary amine group likely exhibits strong adsorption to soil, thereby reducing the bioavailability. In contrast, the amine oxide group imparts high reactivity to PFOSNO, resulting in its rapid biotic and abiotic transformations in soil. The microbial stability ranking also shows that the formation of a precursor to the tertiary amines (PFOSAm or PFOAAm) can be a rate-limiting step, as in the cases of quaternary ammonium and betaine compounds.

Most studies have focused only on the aerobic microbial transformation of *N*-alkyl amine-containing FASAs, with no significant loss of FASAs observed in sterilized controls. Unexpectedly, Chen et al.[88] found that in sterile soils, the concentrations of PFOSNO were significantly decreased, accompanied by production of FOSAA and FOSA at very low yields, which indicated the possibility of abiotic transformation of amine oxides. However, the production of PFSAs has only been observed in live soils.[24,84,88]

3.3. Cationic/Zwitterionic FT-Derivatives. Cationic and zwitterionic fluorotelomer derivatives, including 6:2 fluorotelomer sulfonamido amine oxide (6:2 FTNO), 6:2 FtSaAm, and 6:2 FTAB, are discussed in comparison with their FASA analogues PFOSNO, PFOSAm, and PFOSB, respectively. Overall, the microbial recalcitrance ranking of 6:2 FT sulfonamide-containing PFAS follows the order 6:2 FTAB ≫ 6:2 FtSaAm > 6:2 FTNO,[90] which aligns with the resistance order observed for FASAs with different *N*-alkyl substitutions.[87]

Fang et al.[90] reported rapid microbial transformation of 6:2 FTNO in aerobic sludge, with a half-life of 1.2 days. This aligns with the rapid loss of PFOSNO and PFOANO observed in aerobic soil, attributed to the high reactivity of the amine oxide.[87,88] However, unlike the pronounced and extensive abiotic transformation of PFOSNO and PFOANO in sterilized soil,[88] the abiotic transformation of 6:2 FTNO in sludge was found to be negligible.[90] 6:2 FTNO underwent a series of biotransformation reactions, including N-demethylation, deamination, hydroxylation, oxidation, and decarboxylation, ultimately forming 6:2 fluorotelomer sulfonamide (6:2 FTSAm). Further transformation products like 6:2 FTS and short-chain PFAAs were not detected.[90] This contrasts with the microbial transformation of PFOSNO and PFOANO in soil, which leads to the formation of PFOS and PFOA.[88] 6:2 FTSAm appeared to be resistant to hydrolysis in aerobic sludge.

6:2 FtSaAm was proposed to be a primary intermediate product of 6:2 FTNO, with an estimated microbial transformation half-life of 11.5 days in activated sludge.[90] D'Agostino et al. reported that 6:2 FtSaAm was biotransformed in aerobic sludge, yielding 6:2 fluorotelomer alcohol (6:2 FTOH), 5:3 fluorotelomer carboxylic acid (5:3 FTCA), and short-chain PFAAs, including perfluorohexanoic acid (PFHxA), perfluorobutanoic acid (PFPeA), and perfluorobutanoic acid (PFBA). 6:2 FTOH is a critical intermediate for various fluorotelomer-based precursors.[91,92] Due to the high reactivity of its hydroxyl group, it undergoes oxidative defluorination, ultimately forming PFCAs with shorter fluorinated chains than the parent compound. This is a significant difference from the biotransformation products of FASAs, which have not been observed to undergo microbial partial defluorination and ultimately form PFSAs instead of PFCAs. Notably, 6:2 FtSaAm was found to be transformed into 6:2 FTSAm and 6:2 FTS through abiotic processes in sterilized sludge.

Overall, 6:2 FTAB exhibited a strong recalcitrance to microbes. In the activated sludge reported by Fang et al., the concentration of 6:2 FTAB showed no significant reduction after 100 days of aerobic incubation.[90] D'Agostino et al.[93] reported that in aerobic activated sludge, 6:2 FTAB underwent microbial transformation to produce small amounts of 6:2 FTSAm, 6:2 FTOH, 5:3 FTCA, PFHxA, PFPeA, and PFBA (total molar yield≈ 3%). Similar to 6:2 FtSaAm, 6:2 FTAB underwent abiotic transformation in sterilized sludge to form 6:2 FTSAm (molar yield ≈5%). Interestingly, in petroleum hydrocarbon-amended soil, 6:2 FTAB decreased rapidly, with an estimated half-life of 31 days, and the accumulation of 6:2 fluorotelomer unsaturated acid (6:2 FTUA) and 5:2 ketone was observed.[94] However, no accumulation of PFCAs was detected, due to the slow conversion of 6:2 FTAB to PFCAs or the irreversible adsorption of certain transformation intermediates.[94]

3.4. Enzymes Involved. The limited research on microbial enzymes involved in PFAS biotransformation has focused on fluorotelomers.[91,95−100] No studies have reported on enzymes involved in the microbial transformation of FASAs (enzymes in animals, plants, and humans are outside the scope of this review). Therefore, this study focuses on the previously reported microbial enzymes involved in the transformation and degradation of PFAS, their presumed roles, and research methods (Table 4), aiming to provide background and strategies for future research on the biotransformation enzymes of FASAs.

Many oxygenases have been targets for emerging contaminants, including some PFAAs precursors, due to their broad substrate range and proven activity against various persistent organic pollutants.[101,102] Alkanesulfonate monooxygenase, alkane monooxygenase, nitrilotriacetate monooxygenase, alkane hydroxylase, and cytochrome P450 were found to be upregulated and involved in the biotransformation of 6:2 FTS, 6:2 polyfluoroalkyl phosphates (6:2 PAPs), and 6:2 FTOH.[95,96,98,103] Furthermore, heterologous gene expression experiments in *E. coli* confirmed that cytochrome P450 and alkane monooxygenase possess defluorination activity toward 6:2 FTOH.[96] Crude enzymes of alkanesulfonate monooxygenase (gene: Ssu D and SsuE) were shown to desulfonate 6:2 FTS and produce sulfite.[96] It is noteworthy that the Ssu operon (SsuABC, SsuD, and SsuE) is known to be expressed by certain bacteria to utilize organosulfonates as sulfur sources for growth under sulfur-limiting conditions,[104] which is consistent with the biotransformation of 6:2 FTS by various bacteria under sulfur-limited conditions.[95−97] However, neither of these above-mentioned strains exhibiting desulfonation of 6:2 FTS is able to grow with PFOS or PFHxS as the sole sulfur source.[95,97] In addition to these monooxygenases, Olivares et al.[91] reported the presence of toluene dioxygenase in AFFF-impacted soils, which may be involved in the biotransformation of 6:2 fluorotelomer thioacetic acid sulfonate (6:2 FtTAoS). Moreover, some fluorinated aromatics, fluorinated olefins, and a short-chain ether PFAS (1,1,1,2-tetrafluoro-2-trifluoromethoxy-4-iodobutane) were shown to induce toluene dioxygenase in *Pseudomonas putida* F1.[105] The transformation and defluorination activity of dioxygenases toward PFAS still needs further validation.

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

Haloacid dehalogenases are another class of enzymes that have been found to be involved in the microbial transformation of PFAS. Yang et al.[96] reported that the expression of haloacid dehalogenase in *Rhodococcus jostii* RHA1 was upregulated during the transformation of 6:2 FTOH and 6:2 FTS. Additionally, enzyme inhibition tests and heterologous expression further confirmed that this haloacid dehalogenase exhibits defluorination activity on 6:2 FTOH. Furthermore, Harris et al.[99] introduced a gene (PZP66635.1) encoding haloacid dehalogenases from *Delftia acidovorans* into a plasmid for expression in *Escherichia coli*. The results showed that fluorine ions were detected in the transformed *E. coli* samples incubated with PFOA, although the levels were not significantly different from those in the control group without PFOA.

Recently, a few studies reported the reductive defluorination of α,β-unsaturated per- and polyfluorocarboxylic acids by *Acetobacterium* species under anaerobic conditions.[100,106,107] Yu et al.[100] were the first to demonstrate that the Fluc family F^- channels encoded by crcB1 and crcB2 are involved in transporting fluoride ions out of the cell, a process essential for cellular defluorination activity.[108] Fluoride is toxic to cells as it inactivates essential enzymes, including ATPases, which directly generate energy, and pyrophosphatase, which is critical for maintaining a phosphate source to biosynthesize ATP.[108] Furthermore, Yu et al. reported that caffeoyl-CoA reductase can reduce the α,β-unsaturated bond in (*E*)-perfluoro-4-methylpent-2-enoic acid (PFMeUPA, $(CF_3)_2CFCF{=}CFCOOH$) in a manner similar to its reduction of caffeate, leading to defluorination.[100]

In contrast to fluorotelomers, the final products of microbial transformation of FASAs are PFSAs rather than PFCAs. This indicates that the microbial metabolism of FASAs does not involve desulfonation but involves sulfonamide hydrolysis and assimilation of N-substituents. PFSA yields from N-alkylamine FASAs have been associated with methanotrophy[80,84] and nitrification,[24] both microbial processes that involve well-known cometabolic oxygenase (such as methane monooxygenase, ammonium monooxygenase).[109−113] Methane monooxygenase has been proven to be capable of oxidizing alkanes, alkenes, alicyclics, aromatics, ethers, heterocyclics, chlorinated solvents, and ammonia.[114] A recent study reported that in parallel with the biotransformation of C6-FASAs (FHxSA, PFHxSAm, and PFHxSAmS), there was an increase in the total abundance of nitrifying taxa (such as Nitrososphaeria and Nitrospina) and nitrate concentrations,[24] suggesting associations between nitrification and FASAs biotransformation. There is ample evidence of cometabolism of nonfluorinated sulfonamides in the natural and built environment,[109−113,115,116] although the hydrolysis of the sulfonamide bond is not usually detected. Certain sulfonamide monooxygenases and flavin reductases have been reported to be involved in the initial cleavage reaction of sulfonamides, leading to the breakdown of an S−N bond and the production of sulfur dioxide.[117,118] It is possible that the perfluorocarbon chain adjacent to the sulfonamide group appears to largely hinder sulfonamides hydrolysis. Direct hydrolysis of the sulfonamide bond in N-alcohol or N-carboxylated FASAs has been proposed as an alternate pathway to PFSAs[36,119] and supported by lower activation energy required than for FASA hydrolysis.[24] The NH_2 moiety in FASAs is not a great leaving group, so bacterial hydrolases likely use metals (i.e., Zn^{2+}) or acid to mediate the conjugation of glutathione with the substrate, releasing NH_2. Indeed, glutathione[120] and N-glucuronidation[121] of FASAs have been reported during in vivo transformations in mouse models but have not been evaluated in microbial systems. Yet, bacterial glutathione transferases are well-known enzymatic systems mediating xenobiotic detoxification and oxidative stress.[122] A systematic evaluation of the specific enzymatic activity linked to FASA biotransformation is needed.

Currently, enzymes involved in biotransformation are mainly identified through differential expression of genes or proteins in microbial communities when exposed to PFAS. Heterologous gene expression or purified enzyme activity assays can further verify the enzymatic ability to transform FASAs based on increases of PFSAs in the medium. In vitro tests in which biological enzymes and PFAS are coincubated can directly display the conversion and kinetic characteristics of certain enzymes to the PFAS substrate. Computational methods, including molecular docking, molecular dynamics, and quantum mechanics/molecular mechanics, can help predict the binding affinity of FASAs,[123−127] before experimental validation.

4. RESEARCH GAPS AND PROSPECTS

FASAs differ from fluorotelomers in their diverse charged properties and antibacterial characteristics. This review examined the sorption and microbial transformation of FASAs to clarify their complex environmental fate. Compared with fluorotelomers, FASAs exhibit stronger sorption onto soil and greater resistance to microbial transformation. Despite the slow transformation, the terminal end products, PFSAs, become more mobile. Therefore, the introduction of FASAs into the environment poses longer-term and more widespread pollution issues. Several gaps remain regarding sorption descriptors, biotransformation pathways, and enzymes involved. We suggest the following research directions.

(1) Experimental pK_a and biosorption descriptors. Due to the complex speciation changes of certain FASAs, pK_as significantly influence their adsorption behaviors and microbial bioavailability.[18] However, the pK_a values of FASAs in current studies are mostly predicted by models trained with nonfluorinated compounds. Therefore, experimentally determined pK_a values are necessary for future research to characterize the speciation of FASAs in real environmental media. In addition, the sorption of FASAs by bacteria should be investigated in future research to get a comprehensive understanding of the extent of microbial biosorption in the environment.

(2) The fate of short-chain FASAs and their transformation under anoxic conditions. At present, most studies focus on the fate of C8 FASAs. However, with the gradual phase-out of long-chain PFAS, C6 and C4 FASAs have become more frequently detected in various applications. This has resulted in a significant data gap regarding the sorption and transformation of these short-chain FASAs in environmental media. Additionally, the microbial transformation of FASAs under anoxic conditions also warrants attention. These efforts will contribute to a better understanding of the fate and transport of FASAs in subsurface environments.

(3) Identification of enzymes responsible for biotransformation of FASAs. Current studies on the biotransformation of FASAs have only focused on biotransformation

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

reactions, lacking identification of the microorganisms and enzymes involved in the biotransformation. Simplified microcosms (such as enrichment, pure strains, and cell-derived active mixtures) can be used to test the degradability on FASAs. Additionally, it is essential to elucidate the mechanisms of microbial transformation of FASAs (whether through cometabolism) and identify key biomarkers, including involved enzymes. These efforts will contribute to developing effective remediation strategies for FASAs-impacted sites.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c00906.

The names, acronyms, CAS numbers, and structures of FASAs and their reference compounds and soil characteristics from studies on FASAs adsorption (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Christopher I. Olivares − *Civil & Environmental Engineering, University of California, Irvine, Irvine, California 92697, United States;* orcid.org/0000-0001-6213-7158; Email: chris.olivares@uci.edu

Author

Donghui Ma − *Civil & Environmental Engineering, University of California, Irvine, Irvine, California 92697, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.5c00906

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank SERDP for funding this work under ER23-3827.

■ REFERENCES

(1) Ruyle, B. J.; Thackray, C. P.; McCord, J. P.; Strynar, M. J.; Mauge-Lewis, K. A.; Fenton, S. E.; Sunderland, E. M. Reconstructing the Composition of Per- and Polyfluoroalkyl Substances in Contemporary Aqueous Film-Forming Foams. *Environ. Sci. Technol. Lett.* **2021**, *8* (1), 59−65.

(2) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* **2017**, *51* (4), 2047−2057.

(3) Chu, S.; Letcher, R. J. In Vitro Metabolic Formation of Perfluoroalkyl Sulfonamides from Copolymer Surfactants of Pre- and Post-2002 Scotchgard Fabric Protector Products. *Environ. Sci. Technol.* **2014**, *48* (11), 6184−6191.

(4) Maizel, A.; Thompson, A.; Tighe, M.; Escobar Veras, S.; Rodowa, A.; Falkenstein-Smith, R.; Benner Jr, B. A.; Hoffman, K.; Donnelly, M. K.; Hernandez, O.; Wetzler, N.; Ngu, T.; Reiner, J.; Place, B.; Kucklick, J.; Rimmer, K.; Davis, R. D. *Per- and Polyfluoroalkyl Substances in New Firefighter Turnout Gear Textiles*; National Institute of Standards and Technology (U.S.): 2023; NIST TN 2248. DOI: 10.6028/NIST.TN.2248.

(5) Chen, Y.-J.; Wang, R.-D.; Shih, Y.-L.; Chin, H.-Y.; Lin, A. Y.-C. Emerging Perfluorobutane Sulfonamido Derivatives as a New Trend of Surfactants Used in the Semiconductor Industry. *Environ. Sci. Technol.* **2024**, *58* (3), 1648−1658.

(6) Chen, Y.-J.; Yang, J.-S.; Lin, A. Y.-C. Comprehensive Nontargeted Analysis of Fluorosurfactant Byproducts and Reaction Products in Wastewater from Semiconductor Manufacturing. *Sustain Environ. Res.* **2024**, *34* (1), 14.

(7) Zabaleta, I.; Bizkarguenaga, E.; Nunoo, D. B. O.; Schultes, L.; Leonel, J.; Prieto, A.; Zuloaga, O.; Benskin, J. P. Biodegradation and Uptake of the Pesticide Sulfluramid in a Soil−Carrot Mesocosm. *Environ. Sci. Technol.* **2018**, *52* (5), 2603−2611.

(8) Gluge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Envr. Sci. Proc. Imp.* **2020**, *22* (12), 2345−2373.

(9) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.* **2013**, *47* (15), 8187−8195.

(10) D'Agostino, L. A.; Mabury, S. A. Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates. *Environ. Sci. Technol.* **2014**, *48* (1), 121−129.

(11) Place, B. J.; Field, J. A. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environ. Sci. Technol.* **2012**, *46* (13), 7120−7127.

(12) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47* (10), 5226−5234.

(13) Baduel, C.; Mueller, J. F.; Rotander, A.; Corfield, J.; Gomez-Ramos, M.-J. Discovery of Novel Per- and Polyfluoroalkyl Substances (PFASs) at a Fire Fighting Training Ground and Preliminary Investigation of Their Fate and Mobility. *Chemosphere* **2017**, *185*, 1030−1038.

(14) Ghorbani Gorji, S.; Gómez Ramos, M. J.; Dewapriya, P.; Schulze, B.; Mackie, R.; Nguyen, T. M. H.; Higgins, C. P.; Bowles, K.; Mueller, J. F.; Thomas, K. V.; Kaserzon, S. L. New PFASs Identified in AFFF Impacted Groundwater by Passive Sampling and Nontarget Analysis. *Environ. Sci. Technol.* **2024**, *58* (3), 1690−1699.

(15) Truong, L.; Rericha, Y.; Thunga, P.; Marvel, S.; Wallis, D.; Simonich, M. T.; Field, J. A.; Cao, D.; Reif, D. M.; Tanguay, R. L. Systematic Developmental Toxicity Assessment of a Structurally Diverse Library of PFAS in Zebrafish. *J. Hazard. Mater.* **2022**, *431*, No. 128615.

(16) Britton, K. N.; Judson, R. S.; Hill, B. N.; Jarema, K. A.; Olin, J. K.; Knapp, B. R.; Lowery, M.; Feshuk, M.; Brown, J.; Padilla, S. Using Zebrafish to Screen Developmental Toxicity of Per- and Polyfluoroalkyl Substances (PFAS). *Toxics* **2024**, *12* (7), 501.

(17) Burman, L. G. The Antimicrobial Activities of Trimethoprim and Sulfonamides. *Scand. J. Infect. Dis* **1986**, *18* (1), 3−13.

(18) Rayne, S.; Forest, K. A New Class of Perfluorinated Acid Contaminants: Primary and Secondary Substituted Perfluoroalkyl Sulfonamides Are Acidic at Environmentally and Toxicologically Relevant pH Values. *J. Environ. Sci. Health., Part A* **2009**, *44* (13), 1388−1399.

(19) Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integr Environ. Assess Manag* **2011**, *7* (4), 513−541.

(20) Brusseau, M. L. Influence of Chain Length on Field-Measured Distributions of PFAS in Soil and Soil Porewater. *J,. Hazard Mater. Lett.* **2023**, *4*, No. 100080.

(21) Campos Pereira, H.; Ullberg, M.; Kleja, D. B.; Gustafsson, J. P.; Ahrens, L. Sorption of Perfluoroalkyl Substances (PFASs) to an Organic Soil Horizon − Effect of Cation Composition and pH. *Chemosphere* **2018**, *207*, 183−191.

(22) Cai, W.; Navarro, D. A.; Du, J.; Ying, G.; Yang, B.; McLaughlin, M. J.; Kookana, R. S. Increasing Ionic Strength and Valency of Cations Enhance Sorption through Hydrophobic Interactions of PFAS with Soil Surfaces. *Sci. Total Environ.* **2022**, *817*, No. 152975.
(23) Dai, M.; Yan, N.; Brusseau, M. L. Potential Impact of Bacteria on the Transport of PFAS in Porous Media. *Water Res.* **2023**, *243*, No. 120350.
(24) Ruyle, B. J.; Schultes, L.; Akob, D. M.; Harris, C. R.; Lorah, M. M.; Vojta, S.; Becanova, J.; McCann, S.; Pickard, H. M.; Pearson, A.; Lohmann, R.; Vecitis, C. D.; Sunderland, E. M. Nitrifying Microorganisms Linked to Biotransformation of Perfluoroalkyl Sulfonamido Precursors from Legacy Aqueous Film-Forming Foams. *Environ. Sci. Technol.* **2023**, *57* (14), 5592−5602.
(25) Butzen, M. L.; Wilkinson, J. T.; McGuinness, S. R.; Amezquita, S.; Peaslee, G. F.; Fein, J. B. Sorption and Desorption Behavior of PFOS and PFOA onto a Gram-Positive and a Gram-Negative Bacterial Species Measured Using Particle-Induced Gamma-Ray Emission (PIGE) Spectroscopy. *Chem. Geol.* **2020**, *552*, No. 119778.
(26) Fu, J.; Gao, B.; Xu, H.; Hao, S.; Ren, J.; Wu, J.; Sun, Y. Effects of Biofilms on the Retention and Transport of PFOA in Saturated Porous Media. *J. Hazard Mater.* **2023**, *443*, No. 130392.
(27) Miner, K. R.; Clifford, H.; Taruscio, T.; Potocki, M.; Solomon, G.; Ritari, M.; Napper, I. E.; Gajurel, A. P.; Mayewski, P. A. Deposition of PFAS 'Forever Chemicals' on Mt. Everest. *Sci. Total Environ.* **2021**, *759*, No. 144421.
(28) Huang, S.; Jaffé, P. R. Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) Bby Acidimicrobium Sp. Strain A6. *Environ. Sci. Technol.* **2019**, *53* (19), 11410−11419.
(29) Yi, L.; Peng, Q.; Liu, D.; Zhou, L.; Tang, C.; Zhou, Y.; Chai, L. Enhanced Degradation of Perfluorooctanoic Acid by a Genome Shuffling-Modified Pseudomonas Parafulva YAB-1. *Environ. Technol.* **2019**, *40*, 3153.
(30) Luo, Q.; Liang, S.; Huang, Q. Laccase Induced Degradation of Perfluorooctanoic Acid in a Soil Slurry. *J. Hazard. Mater.* **2018**, *359*, 241−247.
(31) Park, J.; Huang, S.; Koel, B. E.; Jaffé, P. R. Enhanced Feammox Activity and Perfluorooctanoic Acid (PFOA) Degradation by Acidimicrobium Sp. Strain A6 Using PAA-Coated Ferrihydrite as an Electron Acceptor. *J. Hazard. Mater.* **2023**, *459*, No. 132039.
(32) Khan, M. F.; Guin, J. P.; Thampi, R. K.; Sullivan, J. A.; Murphy, C. D. Enhanced Removal of Perfluorooctanoic Acid with Sequential Photocatalysis and Fungal Treatment. *Environ. Sci. Pollut. Res.* **2023**, *30* (39), 91478−91486.
(33) Yan, P.-F.; Dong, S.; Pennell, K. D.; Cápiro, N. L. A Review of the Occurrence and Microbial Transformation of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Film-Forming Foam (AFFF)-Impacted Environments. *Sci. Total Environ.* **2024**, *927*, No. 171883.
(34) Liu, J.; Mejia Avendaño, S. Microbial Degradation of Polyfluoroalkyl Chemicals in the Environment: A Review. *Environ. Int.* **2013**, *61*, 98−114.
(35) Berhanu, A.; Mutanda, I.; Taolin, J.; Qaria, M. A.; Yang, B.; Zhu, D. A Review of Microbial Degradation of Per- and Polyfluoroalkyl Substances (PFAS): Biotransformation Routes and Enzymes. *Sci. Total Environ.* **2023**, *859*, No. 160010.
(36) Choi, Y. J.; Helbling, D. E.; Liu, J.; Olivares, C. I.; Higgins, C. P. Microbial Biotransformation of Aqueous Film-Forming Foam Derived Polyfluoroalkyl Substances. *Sci. Total Environ.* **2022**, *824*, No. 153711.
(37) LaFond, J. A.; Hatzinger, P. B.; Guelfo, J. L.; Millerick, K.; Jackson, W. A. Bacterial Transformation of Per- and Poly-Fluoroalkyl Substances: A Review for the Field of Bioremediation. *Environ, Sci. Adv.* **2023**, *2* (8), 1019−1041.
(38) Geng, F.; Helbling, D. E. Cascading Pathways Regulate the Biotransformations of Eight Fluorotelomer Acids Performed by Wastewater Microbial Communities. *Environ. Sci. Technol.* **2024**, *58* (52), 23201−23211.
(39) Nguyen, T. M. H.; Bräunig, J.; Thompson, K.; Thompson, J.; Kabiri, S.; Navarro, D. A.; Kookana, R. S.; Grimison, C.; Barnes, C. M.; Higgins, C. P.; McLaughlin, M. J.; Mueller, J. F. Influences of Chemical Properties, Soil Properties, and Solution pH on Soil−Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs). *Environ. Sci. Technol.* **2020**, *54* (24), 15883−15892.
(40) Campos-Pereira, H.; Kleja, D. B.; Ahrens, L.; Enell, A.; Kikuchi, J.; Pettersson, M.; Gustafsson, J. P. Effect of pH, Surface Charge and Soil Properties on the Solid−Solution Partitioning of Perfluoroalkyl Substances (PFASs) in a Wide Range of Temperate Soils. *Chemosphere* **2023**, *321*, No. 138133.
(41) Higgins, C. P.; Luthy, R. G. Sorption of Perfluorinated Surfactants on Sediments. *Environ. Sci. Technol.* **2006**, *40* (23), 7251−7256.
(42) Mejia-Avendaño, S.; Zhi, Y.; Yan, B.; Liu, J. Sorption of Polyfluoroalkyl Surfactants on Surface Soils: Effect of Molecular Structures, Soil Properties, and Solution Chemistry. *Environ. Sci. Technol.* **2020**, *54* (3), 1513−1521.
(43) Barzen-Hanson, K. A.; Davis, S. E.; Kleber, M.; Field, J. A. Sorption of Fluorotelomer Sulfonates, Fluorotelomer Sulfonamido Betaines, and a Fluorotelomer Sulfonamido Amine in National Foam Aqueous Film-Forming Foam to Soil. *Environ. Sci. Technol.* **2017**, *51* (21), 12394−12404.
(44) Xiao, F.; Jin, B.; Golovko, S. A.; Golovko, M. Y.; Xing, B. Sorption and Desorption Mechanisms of Cationic and Zwitterionic Per- and Polyfluoroalkyl Substances in Natural Soils: Thermodynamics and Hysteresis. *Environ. Sci. Technol.* **2019**, *53* (20), 11818−11827.
(45) Heinz, H.; Vaia, R. A.; Krishnamoorti, R.; Farmer, B. L. Self-Assembly of Alkylammonium Chains on Montmorillonite: Effect of Chain Length, Head Group Structure, and Cation Exchange Capacity. *Chem. Mater.* **2007**, *19* (1), 59−68.
(46) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. Adsorption and Desorption of Different Organic Matter Fractions on Iron Oxide. *Geochim. Cosmochim. Acta* **1995**, *59* (2), 219−229.
(47) Rayne, S.; Forest, K. Comment on "Indirect Photolysis of Perfluorochemicals: Hydroxyl Radical-Initiated Oxidation of N-Ethyl Perfluorooctane Sulfonamido Acetate (N-EtFOSAA) and Other Perfluoroalkanesulfonamides.". *Environ. Sci. Technol.* **2009**, *43* (20), 7995−7996.
(48) 3M Company. Final Report: Summary of Physical/Chemical and Environmental Parameters for PFAS: Subject to Interim Special Order by Consent No. 20−086-CWP/AP/GW/HW/DW/SW, paragraph 37(J)(3). Laboratory Request Number: E21-0037. Published January 14, 2021. https://rais.ornl.gov/documents/3M.pdf.
(49) Campos-Pereira, H.; Makselon, J.; Kleja, D. B.; Prater, I.; Kögel-Knabner, I.; Ahrens, L.; Gustafsson, J. P. Binding of Per- and Polyfluoroalkyl Substances (PFASs) by Organic Soil Materials with Different Structural Composition − Charge- and Concentration-Dependent Sorption Behavior. *Chemosphere* **2022**, *297*, No. 134167.
(50) Li, L.; Wang, T.; Sun, Y.; Wang, P.; Yvette, B.; Meng, J.; Li, Q.; Zhou, Y. Identify Biosorption Effects of *Thiobacillus* towards Perfluorooctanoic Acid (PFOA): Pilot Study from Field to Laboratory. *Chemosphere* **2017**, *171*, 31−39.
(51) Wu, D.; Tong, M.; Kim, H. Influence of Perfluorooctanoic Acid on the Transport and Deposition Behaviors of Bacteria in Quartz Sand. *Environ. Sci. Technol.* **2016**, *50* (5), 2381−2388.
(52) Fitzgerald, N. J. M.; Wargenau, A.; Sorenson, C.; Pedersen, J.; Tufenkji, N.; Novak, P. J.; Simcik, M. F. Partitioning and Accumulation of Perfluoroalkyl Substances in Model Lipid Bilayers and Bacteria. *Environ. Sci. Technol.* **2018**, *52* (18), 10433−10440.
(53) Jian-Zhou, H.; Cheng-Cheng, L.; Deng-Jun, W.; Zhou, D.-M. Biofilms and Extracellular Polymeric Substances Mediate the Transport of Graphene Oxide Nanoparticles in Saturated Porous Media. *J. Hazard. Mater.* **2015**, *300*, 467−474.
(54) Yan, W.; Qian, T.; Zhang, L.; Wang, L.; Zhou, Y. Interaction of Perfluorooctanoic Acid with Extracellular Polymeric Substances - Role of Protein. *J. Hazard. Mater.* **2021**, *401*, No. 123381.
(55) Wilson, W. W.; Wade, M. M.; Holman, S. C.; Champlin, F. R. Status of Methods for Assessing Bacterial Cell Surface Charge Properties Based on Zeta Potential Measurements. *J. Microb. Met.* **2001**, *43* (3), 153−164.

(56) Harden, V. P.; Harris, J. O. The Isoelectric Point of Bacterial Cells. *J. Bacteriol.* **1953**, *65* (2), 198−202.
(57) Beveridge, T. J.; Murray, R. G. Sites of Metal Deposition in the Cell Wall of Bacillus Subtilis. *J. Bacteriol.* **1980**, *141* (2), 876−887.
(58) Zhou, Q.; Deng, S.; Zhang, Q.; Fan, Q.; Huang, J.; Yu, G. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Activated Sludge. *Chemosphere* **2010**, *81* (4), 453−458.
(59) Presentato, A.; Lampis, S.; Vantini, A.; Manea, F.; Daprà, F.; Zuccoli, S.; Vallini, G. On the Ability of Perfluorohexane Sulfonate (PFHxS) Bioaccumulation by Two Pseudomonas Sp. Strains Isolated from PFAS-Contaminated Environmental Matrices. *Microorganisms* **2020**, *8* (1), 92.
(60) Cheng, W.; Ng, C. A. A Permeability-Limited Physiologically Based Pharmacokinetic (PBPK) Model for Perfluorooctanoic Acid (PFOA) in Male Rats. *Environ. Sci. Technol.* **2017**, *51* (17), 9930−9939.
(61) Nakagawa, H.; Terada, T.; Harada, K.; Hitomi, T.; Inoue, K.; Inui, K. I.; Koizumi, A. Human Organic Anion Transporter hOAT4 is a Transporter of Perfluorooctanoic Acid. *Basic Clin. Pharmacol. Toxicol.* **2009**, *105* (2), 136.
(62) Weaver, Y. M.; Ehresman, D. J.; Butenhoff, J. L.; Hagenbuch, B. Roles of Rat Renal Organic Anion Transporters in Transporting Perfluorinated Carboxylates with Different Chain Lengths. *Toxicol. Sci.* **2010**, *113* (2), 305−314.
(63) Yang, C. H.; Glover, K. P.; Han, X. Characterization of Cellular Uptake of Perfluorooctanoate via Organic Anion-Transporting Polypeptide 1A2, Organic Anion Transporter 4, and Urate Transporter 1 for Their Potential Roles in Mediating Human Renal Reabsorption of Perfluorocarboxylates. *Toxicol. Sci.* **2010**, *117* (2), 294−302.
(64) Yang, S.-F.; Lin, C.-F.; Yu-Chen Lin, A.; Andy Hong, P.-K. Sorption and Biodegradation of Sulfonamide Antibiotics by Activated Sludge: Experimental Assessment Using Batch Data Obtained under Aerobic Conditions. *Water Res.* **2011**, *45* (11), 3389−3397.
(65) Yang, S.-F.; Lin, C.-F.; Wu, C.-J.; Ng, K.-K.; Yu-Chen Lin, A.; Andy Hong, P.-K. Fate of Sulfonamide Antibiotics in Contact with Activated Sludge − Sorption and Biodegradation. *Water Res.* **2012**, *46* (4), 1301−1308.
(66) Pi, S.; Li, A.; Cui, D.; Su, Z.; Feng, L.; Ma, F.; Yang, J. Biosorption Behavior and Mechanism of Sulfonamide Antibiotics in Aqueous Solution on Extracellular Polymeric Substances Extracted from *Klebsiella* Sp. J1. *Bioresour, Biotechnol.* **2019**, *272*, 346−350.
(67) Weathers, T. S.; Higgins, C. P.; Sharp, J. O. Enhanced Biofilm Production by a Toluene-Degrading Rhodococcus Observed after Exposure to Perfluoroalkyl Acids. *Environ. Sci. Technol.* **2015**, *49* (9), 5458−5466.
(68) Gao, J.; Pedersen, J. A. Sorption of Sulfonamide Antimicrobial Agents to Humic Acid−Clay Complexes. *J. Environ. Qual.* **2010**, *39* (1), 228−235.
(69) Tsianou, M.; Bedrov, D.; Alexandridis, P. Surfactants in the Environment: Self-Assembly of PFAS Pollutants in Solution and at Interfaces. In *One Hundred Years of Colloid Symposia: Looking Back and Looking Forward*; American Chemical Society: 2023; pp 443−462. DOI: 10.1021/bk-2023-1457.ch016.
(70) Lange, C. C. *The Aerobic Biodegradation of N-EtFOSE Alcohol by the Microbial Activity Present in Municipal Wastewater Treatment Sludge*, Technical Report for Project CA058, Revised; Pace Analytical Services, Inc. for 3M Environmental Laboratory: 2000.
(71) Boulanger, B.; Vargo, J. D.; Schnoor, J. L.; Hornbuckle, K. C. Evaluation of Perfluorooctane Surfactants in a Wastewater Treatment System and in a Commercial Surface Protection Product. *Environ. Sci. Technol.* **2005**, *39* (15), 5524−5530.
(72) Rhoads, K. R.; Janssen, E. M.-L.; Luthy, R. G.; Criddle, C. S. Aerobic Biotransformation and Fate of N-Ethyl Perfluorooctane Sulfonamidoethanol (N-EtFOSE) in Activated Sludge. *Environ. Sci. Technol.* **2008**, *42* (8), 2873−2878.
(73) Benskin, J. P.; Ikonomou, M. G.; Gobas, F. A. P. C.; Begley, T. H.; Woudneh, M. B.; Cosgrove, J. R. Biodegradation of N-Ethyl Perfluorooctane Sulfonamido Ethanol (EtFOSE) and EtFOSE-Based Phosphate Diester (SAmPAP Diester) in Marine Sediments. *Environ. Sci. Technol.* **2013**, *47* (3), 1381−1389.
(74) Mejia Avendaño, S.; Liu, J. Production of PFOS from Aerobic Soil Biotransformation of Two Perfluoroalkyl Sulfonamide Derivatives. *Chemosphere* **2015**, *119*, 1084−1090.
(75) Zhang, L.; Lee, L. S.; Niu, J.; Liu, J. Kinetic Analysis of Aerobic Biotransformation Pathways of a Perfluorooctane Sulfonate (PFOS) Precursor in Distinctly Different Soils. *Environ. Pollut.* **2017**, *229*, 159−167.
(76) Liu, J.; Zhong, G.; Li, W.; Mejia Avendaño, S. Isomer-Specific Biotransformation of Perfluoroalkyl Sulfonamide Compounds in Aerobic Soil. *Sci. Total Environ.* **2019**, *651*, 766−774.
(77) Peng, H.; Zhang, S.; Sun, J.; Zhang, Z.; Giesy, J. P.; Hu, J. Isomer-Specific Accumulation of Perfluorooctanesulfonate from (N-Ethyl Perfluorooctanesulfonamido)Ethanol-Based Phosphate Diester in Japanese Medaka (Oryzias Latipes). *Environ. Sci. Technol.* **2014**, *48* (2), 1058−1066.
(78) Brusseau, M. L.; Anderson, R. H.; Guo, B. PFAS Concentrations in Soils: Background Levels versus Contaminated Sites. *Sci. Total Environ.* **2020**, *740*, No. 140017.
(79) Liu, T.; Hu, L.-X.; Han, Y.; Dong, L.-L.; Wang, Y.-Q.; Zhao, J.-H.; Liu, Y.-S.; Zhao, J.-L.; Ying, G.-G. Non-Target and Target Screening of per- and Polyfluoroalkyl Substances in Landfill Leachate and Impact on Groundwater in Guangzhou, China. *Sci. Total Environ.* **2022**, *844*, No. 157021.
(80) Yin, T.; Te, S. H.; Reinhard, M.; Yang, Y.; Chen, H.; He, Y.; Gin, K. Y.-H. Biotransformation of Sulfluramid (N-Ethyl Perfluorooctane Sulfonamide) and Dynamics of Associated Rhizospheric Microbial Community in Microcosms of Wetland Plants. *Chemosphere* **2018**, *211*, 379−389.
(81) Murrell, J. C.; Radajewski, S. Cultivation-independent techniques for studying methanotroph ecology. *Res. Microbiol.* **2000**, *151* (10), 807−814.
(82) Pfiffner, S. M.; Palumbo, A. V.; Phelps, T. J.; Hazen, T. C. Effects of nutrient dosing on subsurface methanotrophic populations and trichloroethylene degradation. *J. Ind. Microbiol. Biotechnol.* **1997**, *18* (2−3), 204−212.
(83) Lange, C. C. Anaerobic Biotransformation of N-Methyl Perfluorobutanesulfonamido Ethanol and N-Ethyl Perfluorooctanesulfonamido Ethanol. *Environ. Toxicol. Chem.* **2017**, *37* (3), 768−779.
(84) Cook, E. K.; Olivares, C. I.; Antell, E. H.; Yi, S.; Nickerson, A.; Choi, Y. J.; Higgins, C. P.; Sedlak, D. L.; Alvarez-Cohen, L. Biological and Chemical Transformation of the Six-Carbon Polyfluoroalkyl Substance N-Dimethyl Ammonio Propyl Perfluorohexane Sulfonamide (AmPr-FHxSA). *Environ. Sci. Technol.* **2022**, *56* (22), 15478−15488.
(85) D'Agostino, L. A.; Mabury, S. A. Certain Perfluoroalkyl and Polyfluoroalkyl Substances Associated with Aqueous Film Forming Foam Are Widespread in Canadian Surface Waters. *Environ. Sci. Technol.* **2017**, *51* (23), 13603−13613.
(86) Mejia-Avendaño, S.; Vo Duy, S.; Sauvé, S.; Liu, J. Generation of Perfluoroalkyl Acids from Aerobic Biotransformation of Quaternary Ammonium Polyfluoroalkyl Surfactants. *Environ. Sci. Technol.* **2016**, *50* (18), 9923−9932.
(87) Liu, M.; Munoz, G.; Vo Duy, S.; Sauvé, S.; Liu, J. Stability of nitrogen-containing polyfluoroalkyl substances in aerobic soils. *Environ. Sci. Technol.* **2021**, *55* (8), 4698−4708.
(88) Chen, H.; Liu, M.; Munoz, G.; Duy, S. V.; Sauvé, S.; Yao, Y.; Sun, H.; Liu, J. Fast Generation of Perfluoroalkyl Acids from Polyfluoroalkyl Amine Oxides in Aerobic Soils. *Environ. Sci. Technol. Lett.* **2020**, *7* (10), 714−720.
(89) Rayne, S.; Forest, K. Modeling the Hydrolysis of Perfluorinated Compounds Containing Carboxylic and Phosphoric Acid Ester Functions and Sulfonamide Groups. *J. Environ. Sci. Health., Part A* **2010**, *45* (4), 432−446.
(90) Fang, B.; Zhang, Y.; Chen, H.; Qiao, B.; Yu, H.; Zhao, M.; Gao, M.; Li, X.; Yao, Y.; Zhu, L.; Sun, H. Stability and Biotransformation of 6:2 Fluorotelomer Sulfonic Acid, Sulfonamide Amine Oxide, and

Sulfonamide Alkylbetaine in Aerobic Sludge. *Environ. Sci. Technol.* **2024**, *58*, 2446.
(91) Olivares, C. I.; Yi, S.; Cook, E. K.; Choi, Y. J.; Montagnolli, R.; Byrne, A.; Higgins, C. P.; Sedlak, D. L.; Alvarez-Cohen, L. Aerobic BTEX Biodegradation Increases Yield of Perfluoroalkyl Carboxylic Acids from Biotransformation of a Polyfluoroalkyl Surfactant, 6:2 FtTAoS. *Environ. Sci.: Proc. Imp.* **2022**, *24* (3), 439−446.
(92) Wang, N.; Liu, J.; Buck, R. C.; Korzeniowski, S. H.; Wolstenholme, B. W.; Folsom, P. W.; Sulecki, L. M. 6:2 Fluorotelomer Sulfonate Aerobic Biotransformation in Activated Sludge of Waste Water Treatment Plants. *Chemosphere* **2011**, *82* (6), 853−858.
(93) D'Agostino, L. A.; Mabury, S. A. Aerobic Biodegradation of 2 Fluorotelomer Sulfonamide−Based Aqueous Film−Forming Foam Components Produces Perfluoroalkyl Carboxylates. *Environ. Toxicol. Chem.* **2017**, *36* (8), 2012−2021.
(94) Li, R.; Munoz, G.; Liu, Y.; Sauvé, S.; Ghoshal, S.; Liu, J. Transformation of novel polyfluoroalkyl substances (PFASs) as co-contaminants during biopile remediation of petroleum hydrocarbons. *J. Hazard. Mater.* **2019**, *362*, 140−147.
(95) Méndez, V.; Holland, S.; Bhardwaj, S.; McDonald, J.; Khan, S.; O'Carroll, D.; Pickford, R.; Richards, S.; O'Farrell, C.; Coleman, N.; Lee, M.; Manefield, M. J. Aerobic Biotransformation of 6:2 Fluorotelomer Sulfonate by *Dietzia Aurantiaca* J3 under Sulfur-Limiting Conditions. *Sci. Total Environ.* **2022**, *829*, No. 154587.
(96) Yang, S.-H.; Shi, Y.; Strynar, M.; Chu, K.-H. Desulfonation and Defluorination of 6:2 Fluorotelomer Sulfonic Acid (6:2 FTSA) by Rhodococcus Jostii RHA1: Carbon and Sulfur Sources, Enzymes, and Pathways. *J. Hazard. Mater.* **2022**, *423*, No. 127052.
(97) Van Hamme, J. D.; Bottos, E. M.; Bilbey, N. J.; Brewer, S. E. Genomic and Proteomic Characterization of Gordonia Sp. NB4−1Y in Relation to 6 : 2 Fluorotelomer Sulfonate Biodegradation. *Microbiology* **2013**, *159*, 1618−1628.
(98) Lewis, M.; Kim, M. H.; Liu, E. J.; Wang, N.; Chu, K.-H. Biotransformation of 6:2 Polyfluoroalkyl Phosphates (6:2 PAPs): Effects of Degradative Bacteria and Co-Substrates. *J. Hazard. Mater.* **2016**, *320*, 479−486.
(99) Harris, J. D.; Coon, C. M.; Doherty, M. E.; McHugh, E. A.; Warner, M. C.; Walters, C. L.; Orahood, O. M.; Loesch, A. E.; Hatfield, D. C.; Sitko, J. C.; Almand, E. A.; Steel, J. J. Engineering and Characterization of Dehalogenase Enzymes from Delftia Acidovorans in Bioremediation of Perfluorinated Compounds. *Synthetic and Systems Biotechnology* **2022**, *7* (2), 671−676.
(100) Yu, Y.; Xu, F.; Zhao, W.; Thoma, C.; Che, S.; Richman, J. E.; Jin, B.; Zhu, Y.; Xing, Y.; Wackett, L.; Men, Y. Electron Bifurcation and Fluoride Efflux Systems Implicated in Defluorination of Perfluorinated Unsaturated Carboxylic Acids by Acetobacterium Spp. *Science Advances* **2024**, *10* (29), No. eado2957.
(101) Harayama, S.; Kok, M.; Neidle, E. L. Functional and Evolutionary Relationships among Diverse Oxygenases. *Annu. Rev. Microbiol.* **1992**, *46*, 565−601.
(102) Guo, W.; Ren, H.; Jin, Y.; Chai, Z.; Liu, B. The Bioremediation of the Typical Persistent Organic Pollutants (POPs) by Microalgae-Bacteria Consortia: A Systematic Review. *Chemosphere* **2024**, *355*, No. 141852.
(103) Ricken, B.; Kolvenbach, B. A.; Bergesch, C.; Benndorf, D.; Kroll, K.; Strnad, H.; Vlček, Č.; Adaixo, R.; Hammes, F.; Shahgaldian, P.; Schäffer, A.; Kohler, H.-P. E.; Corvini, P. F.-X. FMNH2-Dependent Monooxygenases Initiate Catabolism of Sulfonamides in Microbacterium Sp. Strain BR1 Subsisting on Sulfonamide Antibiotics. *Sci. Rep* **2017**, *7* (1), No. 15783.
(104) Kahnert, A.; Vermeij, P.; Wietek, C.; James, P.; Leisinger, T.; Kertesz, M. A. The Ssu Locus Plays a Key Role in Organosulfur Metabolism in Pseudomonas putidaS-313. *J. Bacteriol.* **2000**, *182* (10), 2869−2878.
(105) Aukema, K. G.; Bygd, M. D.; Tassoulas, L. J.; Richman, J. E.; Wackett, L. P. Fluoro-Recognition: New in Vivo Fluorescent Assay for Toluene Dioxygenase Probing Induction by and Metabolism of Polyfluorinated Compounds. *Environ.l Microbiol.* **2022**, *24* (11), 5202−5216.
(106) Yu, Y.; Che, S.; Ren, C.; Jin, B.; Tian, Z.; Liu, J.; Men, Y. Microbial Defluorination of Unsaturated Per- and Polyfluorinated Carboxylic Acids under Anaerobic and Aerobic Conditions: A Structure Specificity Study. *Environ. Sci. Technol.* **2022**, *56* (8), 4894−4904.
(107) Yu, Y.; Zhang, K.; Li, Z.; Ren, C.; Chen, J.; Lin, Y.-H.; Liu, J.; Men, Y. Microbial Cleavage of C−F Bonds in Two C6 Per- and Polyfluorinated Compounds via Reductive Defluorination. *Environ. Sci. Technol.* **2020**, *54* (22), 14393−14402.
(108) Wackett, L. P. Why Is the Biodegradation of Polyfluorinated Compounds So Rare? *mSphere* **2021**, *6* (5), 1.
(109) Zhou, L.-J.; Han, P.; Yu, Y.; Wang, B.; Men, Y.; Wagner, M.; Wu, Q. L. Cometabolic Biotransformation and Microbial-Mediated Abiotic Transformation of Sulfonamides by Three Ammonia Oxidizers. *Water Res.* **2019**, *159*, 444−453.
(110) Lopez Gordillo, A. P.; Trueba-Santiso, A.; Lema, J. M.; Schäffer, A.; Smith, K. E. C. Sulfamethoxazole Is Metabolized and Mineralized at Extremely Low Concentrations. *Environ. Sci. Technol.* **2024**, *58* (22), 9723−9730.
(111) Song, H.-L.; Lu, Y.-X.; Yang, X.-L.; Xu, H.; Singh, R. P.; Du, K.-X.; Yang, Y.-L. Degradation of Sulfamethoxazole in Low-C/N Ratio Wastewater by a Novel Membrane Bioelectrochemical Reactor. *Bioresour. Technol.* **2020**, *305*, No. 123029.
(112) Vega, M. A. P.; Scholes, R. C.; Brady, A. R.; Daly, R. A.; Narrowe, A. B.; Vanzin, G. F.; Wrighton, K. C.; Sedlak, D. L.; Sharp, J. O. Methane-Oxidizing Activity Enhances Sulfamethoxazole Biotransformation in a Benthic Constructed Wetland Biomat. *Environ. Sci. Technol.* **2023**, *57* (18), 7240−7253.
(113) Kassotaki, E.; Buttiglieri, G.; Ferrando-Climent, L.; Rodriguez-Roda, I.; Pijuan, M. Enhanced Sulfamethoxazole Degradation through Ammonia Oxidizing Bacteria Co-Metabolism and Fate of Transformation Products. *Water Res.* **2016**, *94*, 111−119.
(114) Jiang, H.; Chen, Y.; Jiang, P.; Zhang, C.; Smith, T. J.; Murrell, J. C.; Xing, X.-H. Methanotrophs: Multifunctional Bacteria with Promising Applications in Environmental Bioengineering. *Biochem. Engr. J.* **2010**, *49* (3), 277−288.
(115) Wei, C.-H.; Sanchez-Huerta, C.; Leiknes, T.; Amy, G.; Zhou, H.; Hu, X.; Fang, Q.; Rong, H. Removal and Biotransformation Pathway of Antibiotic Sulfamethoxazole from Municipal Wastewater Treatment by Anaerobic Membrane Bioreactor. *J. Hazard. Mater.* **2019**, *380*, No. 120894.
(116) Ghattas, A.-K.; Fischer, F.; Wick, A.; Ternes, T. A. Anaerobic Biodegradation of (Emerging) Organic Contaminants in the Aquatic Environment. *Water Res.* **2017**, *116*, 268−295.
(117) Kim, D.-W.; Thawng, C. N.; Lee, K.; Wellington, E. M. H.; Cha, C.-J. A Novel Sulfonamide Resistance Mechanism by Two-Component Flavin-Dependent Monooxygenase System in Sulfonamide-Degrading Actinobacteria. *Environ. Int.* **2019**, *127*, 206−215.
(118) Ricken, B.; Kolvenbach, B. A.; Bergesch, C.; Benndorf, D.; Kroll, K.; Strnad, H.; Vlček, Č.; Adaixo, R.; Hammes, F.; Shahgaldian, P.; Schäffer, A.; Kohler, H.-P. E.; Corvini, P. F.-X. FMNH2-Dependent Monooxygenases Initiate Catabolism of Sulfonamides in Microbacterium Sp. Strain BR1 Subsisting on Sulfonamide Antibiotics. *Sci. Rep* **2017**, *7* (1), No. 15783.
(119) Rayne, S.; Forest, K. Modeling the Hydrolysis of Perfluorinated Compounds Containing Carboxylic and Phosphoric Acid Ester Functions, Alkyl Iodides, and Sulfonamide Groups. *Nat. Prec* **2009**, 1−1.
(120) Zhao, S.; Wang, B.; Zhong, Z.; Liu, T.; Liang, T.; Zhan, J. Contributions of Enzymes and Gut Microbes to Biotransformation of Perfluorooctane Sulfonamide in Earthworms (*Eisenia Fetida*). *Chemosphere* **2020**, *238*, No. 124619.
(121) Dukes, D. A.; McDonough, C. A. N-glucuronidation and Excretion of Perfluoroalkyl Sulfonamides in Mice Following Ingestion of Aqueous Film-Forming Foam. *Environ. Toxicol. Chem.* **2024**, *43* (11), 2274−2284.

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749

(122) Allocati, N.; Federici, L.; Masulli, M.; Di Ilio, C. Glutathione Transferases in Bacteria. *FEBS Journal* **2009**, *276* (1), 58−75.
(123) Ng, C. A.; Hungerbuehler, K. Exploring the use of molecular docking to identify bioaccumulative perfluorinated alkyl acids (PFAAs). *Environ. Sci. Technol.* **2015**, *49* (20), 12306−12314.
(124) Cheng, W.; Doering, J. A.; LaLone, C.; Ng, C. Integrative Computational Approaches to Inform Relative Bioaccumulation Potential of Per- and Polyfluoroalkyl Substances Across Species. *Toxicol. Sci.* **2021**, *180* (2), 212−223.
(125) Wang, J.; Ilie, A.; Yuan, S.; Reetz, M. T. Investigating Substrate Scope and Enantioselectivity of a Defluorinase by a Stereochemical Probe. *J. Am. Chem. Soc.* **2017**, *139* (32), 11241−11247.
(126) Zhao, L.; Teng, M.; Zhao, X.; Li, Y.; Sun, J.; Zhao, W.; Ruan, Y.; Leung, K. M. Y.; Wu, F. Insight into the Binding Model of Per- and Polyfluoroalkyl Substances to Proteins and Membranes. *Environ. Int.* **2023**, *175*, No. 107951.
(127) Yang, D.; Han, J.; Hall, D. R.; Sun, J.; Fu, J.; Kutarna, S.; Houck, K. A.; LaLone, C. A.; Doering, J. A.; Ng, C. A.; Peng, H. Nontarget Screening of Per- and Polyfluoroalkyl Substances Binding to Human Liver Fatty Acid Binding Protein. *Environ. Sci. Technol.* **2020**, *54* (9), 5676−5686.

https://doi.org/10.1021/acs.est.5c00906
Environ. Sci. Technol. 2025, 59, 10734−10749