

Supplementary materials

Insights into the occurrence, ecotoxicity, and biodegradation of perfluorooctanoic acid and perfluorooctanesulfonic acid in the marine environment

Wenlu Li^{1,2}, Fanping Meng (✉)^{1,2}

1 Key Laboratory of Marine Environment and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China

2 College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

Table S1 Abbreviations used in this review.

Acronym	Chemical name	Acronym	Chemical name
FOSA	Perfluorooctane sulfonamide	TFA	Trifluoroacetic acid
6:2 FTOH	6:2 Fluorine tuned polyol	PFASs	Perfluoroalkanesulfonic acids
8:2 FTOH	8:2 Fluorine tuned polyol	PFOS	Perfluorooctanesulfonic acid
5:3 FTCA	5:3 Fluorotrimeric carboxylic acid	PFHpS	Perfluoroheptanesulfonic acid
PFAS	Per- and polyfluoroalkyl substances	PFHxS	Perfluorohexanesulfonic acid
PFAAs	Perfluoroalkyl acids	PFPeS	Perfluoropentane sulfonic acid
PFCAs	Perfluoroalkyl carboxylic acids	PFBS	Perfluoroalkyl sulfonatic acid
PFOA	Perfluorooctanoic acid	TFA	Trifluoroacetic acid
PFHpA	Perfluoroheptanoic acid	PFASs	Perfluoroalkane sulfonic acids
PFHxA	Perfluorohexanoic acid	HFBA	Heptafluorobutyric acid
PFPeA	Perfluoropentanoic acid	PFPrA	Pentafluoropropionic acid
PFBA	Perfluorobutanoic acid	ROS	Reactive oxygen species
PFPrA	Perfluoropropanoic acid	SOD	Superoxide dismutase
CAT	Catalase		

✉ Corresponding author
E-mail: mengfanping@ouc.edu.cn

Table S2 PFOS and PFOA contents in different marine organisms.

Category	Marine organisms	Organ	Sampling site	PFOA (ng/g) (ww)	PFOS (ng/g) (ww)	Reference
Mixed	-	Whole body	Eastern Canadian Arctic	2.6 ± 0.3	1.8 ± 0.3	(Tomy et al., 2004)
Plankton	-	Whole body	Northwestern Atlantic Margin	0.01-0.16	0.26-3.73	(Zhang et al., 2019)
Mollusk	<i>Mytilus galloprovincialis</i>	Whole body	Portuguese estuaries	-	36.8–125.9	(Cunha et al., 2005)
	<i>Mytilus galloprovincialis</i>	Soft tissues	Northern Spanish coast	-	ND–2.4	(Zabaleta et al., 2015)
	<i>Mya truncata; Serripes groenlandica</i>	Whole body	Eastern Canadian Arctic	-	0.28 ± 0.09	(Tomy et al., 2004)
	<i>Crassostrea gigas</i>	Whole body	Tokyo Bay, Japan	0.66	0.586	(So et al., 2006)
	<i>Perna viridis</i>	Whole body	East Chinese Coast	<0.204–0.328 ± 0.0136	0.114–0.352	(So et al., 2006)
Crustacean	<i>Pandalus borealis; Hymenodora glacialis</i>	Whole body	Eastern Canadian Arctic	0.17 ± 0.06	0.35 ± 0.15	(Tomy et al., 2004)
Fish	<i>Boreogadus saida</i>	Whole body	Eastern Canadian Arctic	0.16 ± 0.06	1.3 ± 0.7	(Tomy et al., 2004)
	<i>Sebastes mentella</i>	Liver	Eastern Canadian Arctic	ND-5.3	ND-6.3	(Tomy et al., 2004)
	<i>Catostomus commersoni</i>	Liver	Arctic	<2	6.5-8.6	(Martin et al., 2004)
	<i>Chelon labrosus</i>	Liver	Northern Spanish coast		24-1062	(Zabaleta et al., 2015)
	<i>Thunnus albacares</i>	Muscle	Indian Ocean	-	ND	(Zabaleta et al., 2015)
	<i>Clupea harengus membras</i>	Muscle	Baltic sub-basins	<0.33–1.20	1.90-3.40	(Kumar et al., 2022)
	<i>Coregonus albula</i>	Muscle	Bothnian bay	-	2.70	(Junttila et al., 2019)
	<i>Clupea harengus membras</i>	Muscle	Baltic Sea	0.07	3.4	(Junttila et al., 2019)
	<i>Perca fluviatilis</i>	Muscle	Baltic Sea	0.03	0.49	(Junttila et al., 2019)
	<i>Gadus morhua</i>	Liver	Baltic Sea	0.1-0.52	6.03-23.9	(Schultes et al., 2020)
Mammal	<i>Delphinapterus leucas</i>	Liver	Eastern Canadian Arctic	1.6 ± 0.3	12.6 ± 1.1	(Tomy et al., 2004)
	<i>Monodon monoceros</i>	Liver	Eastern Canadian Arctic	0.9 ± 0.1	10.9 ± 2.3	(Tomy et al., 2004)

<i>Oxynotus centrina</i>	Muscle	Eastern Mediterranean Sea	0.2	2.8	(Zafeiraki et al., 2019)
	Liver		3.9	20.5	
<i>Heptranchias perlo</i>	Muscle	Eastern Mediterranean Sea	<LOQ	1.0	(Zafeiraki et al., 2019)
	Gills		<LOQ	1.8	
	Liver		<LOQ	3.6	
	Gonads		<LOQ	3.8	
	Heart		<LOQ	2.9	
<i>Phoca vitulina</i>	Liver	German Bight	0.3-3.3	367-577	(Ahrens et al., 2009)

ww=wet weight; ND=not detected; LOQ=limit of quantitation.

Table S3 GESAMP classification of chemicals for acute toxicity (GESAMP, 2013).

Classification	LC ₅₀ /EC ₅₀ (mg/L)	Toxicity rating
0	> 1000	Non-toxic
1	> 100 - ≤ 1000	Practically non-toxic
2	> 10 - ≤ 100	Slightly toxic
3	> 1 - ≤ 10	Moderately toxic
4	> 0.1 - ≤ 1	Highly toxic
5	> 0.01 - ≤ 0.1	Very highly toxic
6	≤ 0.01	Extremely toxic

Table S4 Biodegradation of PFOA and PFOS by microorganisms isolated from various environmental matrices.

Type	Microbial strain	Separation Matrix	Conditions	Initial concentration (mg/L)	Duration (d)	Degradation efficiency (%)	Transformation product	Reference
Fungi	<i>Mucor circinelloides</i>	Soil	28°C	PFOA: 500	3	28.12	-	(Zhou et al., 2019)
	<i>Trichoderma asperellum</i>	Soil	28°C	PFOA: 500	3	24.24	-	(Zhou et al., 2019)
	<i>Pseudeurotium</i> sp. (99% similarity)	Groundwater	Aerobic, 30°C	PFOS: 100	28	29.2	-	(Tseng, 2012)
	<i>Geomyces</i> sp. (99% similarity)	Groundwater	Aerobic, 30°C	PFOA: 100 PFOS: 100	14 14	13.4 17.7	-	(Tseng, 2012)
Bacteria	<i>Pseudomonas aeruginosa</i> HJ4	Activated sludge	Aerobic, pH 7, 35°C	PFOS: 600	2	67	PFBS, PFHxS	(Kwon et al., 2014)
	<i>Pseudomonas parafulva</i> YAB1	Soil	Aerobic, pH 7, 30°C, glucose	PFOA: 500	4	48.1	-	(Yi et al., 2016)
	<i>Pseudomonas plecoglossicida</i> 2.4-D	Soil	Aerobic, pH 7, 28°C	PFOS: 1000	90	75	-	(Chetverikov et al., 2017)
				PFOS: 1000	6	100	PFHpA, F ⁻	
	<i>Pseudomonas aeruginosa</i>	-	Aerobic, 37°C	PFOA: 0.1 PFOS: 0.1	4 4	27.9 47.3	PFHxA PFHxA, PFHpA	(Chiriac et al., 2023)
	<i>Pseudomonas putida</i>	-	Aerobic, 37°C	PFOA: 0.1	4	19	PFPeA, PFHxA,	(Chiriac et al., 2023)
				PFOS: 0.1	4	46.9	PFHpA PFHxA, PFHpA	
	<i>Ensifer adhaerens</i> Strain	Soil	Aerobic, 26°C, pH	PFOA: 1000	4	-	PFHpA, F ⁻	(Chetverikov and

M1		6-8	PFOS: 1000	6	-	PFHpA, F ⁻	Login, 2019)
<i>Acidimicrobium</i> sp. A6	Continuous-flow membrane reactor	Anaerobic, pH 4.5-5, 30°C	PFOA: 0.1 PFOA: 100 PFOS: 0.1 PFOS: 100	100 100 100 100	63 50 60 47	HFBA, PFPeA, PFHxA, PFHpA	(Huang et al., 2019)
<i>Acidimicrobium</i> sp. A6	Continuous-flow membrane reactor	Anaerobic, pH -5-5.5	PFOA: 47	18	77	PFBA, PFPeA, PFHxA, PFHpA, F ⁻	(Ruiz-Urigüen et al., 2022)
<i>Acidimicrobium</i> sp. A6	Continuous-flow membrane reactor	Anaerobic, pH 4.5-5, 25°C	PFOA: 10	150	50	PFBA, PFPeA, PFHxA, PFHpA, F ⁻	(Huang et al., 2022)
<i>Acidimicrobium</i> sp. A6	-	Anaerobic, 25°C, inorganic Fe (III)-NH ₄ ⁺ enrichment medium	PFOA: 0.1 PFOS: 0.1	120 120	46.2 40.1	Shorter carbon-chain PFAAs	(Huang et al., 2024)
Microbial communities in anaerobic digestion	Granular Sludge	Anaerobic, pH 6, 35°C	PFOS: 100	10	24	C ₇ F ₁₅ SO ₃ H, C ₇ F ₁₅ H, C ₇ F ₁₅ CHO, C ₄ F ₉ CHO	(de S. Furtado et al. 2023)

References

- Ahrens L, Siebert U, Ebinghaus R (2009). Temporal trends of polyfluoroalkyl compounds in harbor seals (*Phoca vitulina*) from the German bight, 1999–2008. *Chemosphere*, 76(2): 151-158.
- Chetverikov S P, Sharipov D A, Korshunova T Y, Loginov O N (2017). Degradation of perfluorooctanyl sulfonate by strain *Pseudomonas plecoglossicida* 2.4-D. *Applied Biochemistry and Microbiology*, 53(5), 533-538.
- Chetverikov S P, Loginov O N (2019). A new ensifer adhaerens strain ml is capable of transformation of perfluorocarboxylic acids. *Microbiology*, 88(1), 115-117.
- Chiriac F L, Stoica C, Iftode C, Pirvu F, Petre V A, Paun I, Pascu L F, Vasile G G, Nita-Lazar M (2023). Bacterial biodegradation of perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) using pure *Pseudomonas* strains. *Sustainability*, 15(18): 14000.
- Cunha I, Hoff P, Van de Vijver K, Guilhermino L, Esmans E, De Coen W (2005). Baseline study of perfluorooctane sulfonate occurrence in mussels, *Mytilus galloprovincialis*, from north-central Portuguese estuaries. *Marine Pollution Bulletin*, 50(10): 1128-1132.
- de S. Furtado R X, Sabatini C A, Sakamoto I K, Zaiat M, Azevedo E B (2023). Biodegradation mechanism of perfluorooctane sulfonic acid (PFOS) in domestic sewage: specific methanogenic activity, molecular biology, and ecotoxicological aspects. *Journal of Water Process Engineering*, 51: 103453.
- GESAMP (2013) Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships, 2nd Edition.
- Huang S, Jaffé P R (2019). Defluorination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by *Acidimicrobium* sp. strain A6. *Environmental Science and Technology*, 53(19): 11410-11419.
- Huang S, Sima M, Long Y, Messenger C, Jaffé P R (2022). Anaerobic degradation of perfluorooctanoic acid (PFOA) in biosolids by *Acidimicrobium* sp. strain A6. *Journal of Hazardous Materials*, 424: 127699.

- Huang S, Pilloni G, Key T A, Jaffé P R (2024). Defluorination of various perfluoro alkyl acids and selected PFOA and PFOS monomers by *Acidimicrobium* sp. strain A6 enrichment cultures. *Journal of Hazardous Materials*, 480: 136426.
- Junttila V, Vähä E, Perkola N, Räike A, Siimes K, Mehtonen J, Kankaanpää H, Mannio J (2019). PFASs in Finnish rivers and fish and the loading of PFASs to the Baltic Sea. *Water*, 11(4): 870.
- Kumar E, Koponen J, Rantakokko P, Airaksinen R, Ruokojärvi P, Kiviranta H, Vuorinen P J, Myllylä T, Keinänen M, Raitaniemi J, Mannio J, Junttila V, Nieminen J, Venäläinen E R, Jestoi M (2022). Distribution of perfluoroalkyl acids in fish species from the Baltic Sea and freshwaters in Finland. *Chemosphere*, 291: 132688.
- Kwon B G, Lim H J, Na S H, Choi B I, Shin D S, Chung S Y (2014). Biodegradation of perfluorooctanesulfonate (PFOS) as an emerging contaminant. *Chemosphere*, 109: 221-225.
- Martin J W, Smithwick M M, Braune B M, Hoekstra P F, Muir D C, Mabury S A (2004). Identification of long-chain perfluorinated acids in Biota from the Canadian Arctic. *Environmental Science and Technology*, 38(2): 373-380.
- Ruiz-Urigüen M, Shuai W, Huang S, Jaffé P R (2022). Biodegradation of PFOA in microbial electrolysis cells by *Acidimicrobiaceae* sp. strain A6. *Chemosphere*, 292: 133506.
- Tomy G T, Budakowski W, Halldorson T, Helm P A, Stern G A, Friesen K, Pepper K, Tittlemier S A, Fisk A T (2004). Fluorinated organic compounds in an Eastern Arctic marine food web. *Environmental Science and Technology*, 38(24): 6475-6481.
- Tseng S L (2012). Feasibility of biodegradation of polyfluoroalkyl and perfluoroalkyl substances. University of California, Los Angeles.
- Schultes L, Sandblom O, Broeg K, Bignert A, Benskin J P (2020). Temporal trends (1981-2013) of per- and polyfluoroalkyl substances and total fluorine in Baltic Cod (*Gadus morhua*). *Environmental Toxicology and Chemistry*, 39(2): 300-309.

- So M K, Taniyasu S, Lam P K S, Zheng G J, Giesy J P, Yamashita N (2006). Alkaline digestion and solid phase extraction method for perfluorinated compounds in mussels and oysters from South China and Japan. *Archives of Environmental Contamination and Toxicology*, 50(2): 240-248.
- Yi L B, Chai L Y, Xie Y, Peng Q J, Peng Q Z (2016). Isolation, identification, and degradation performance of a PFOA-degrading strain. *Genetics and Molecular Research*, 15(2), 15028043.
- Zabaleta I, Bizkarguenaga E, Prieto A, Ortiz-Zarragoitia M, Fernández L A, Zuloaga O. (2015). Simultaneous determination of perfluorinated compounds and their potential precursors in mussel tissue and fish muscle tissue and liver samples by liquid chromatography–electrospray-tandem mass spectrometry. *Journal of Chromatography A*, 1387, 13-23.
- Zafeiraki E, Gebbink W A, van Leeuwen S P J, Dassenakis E, Megalofonou P (2019). Occurrence and tissue distribution of perfluoroalkyl substances (PFASs) in sharks and rays from the eastern Mediterranean Sea. *Environmental Pollution*, 252, 379-387.
- Zhang X, Lohmann R, Sunderland E M (2019). Poly- and perfluoroalkyl substances in seawater and plankton from the northwestern Atlantic margin. *Environmental Science & Technology*, 53(21), 12348-12356.
- Zhou L L, Peng Q Z, Xiong L, Yi L B, Peng Q Z, Xiong L, Yi L B (2019). Isolation and identification of perfluorooctanoic acid-degrading fungi. *Chinese Journal of Microecology*, 31(03), 249-253.