Congener-Specific Numbering Systems for the Environmentally Relevant C₄ through C₈ Perfluorinated Homologue Groups of Alkyl Sulfonates, Carboxylates, Telomer Alcohols and Acids and Their Derivatives

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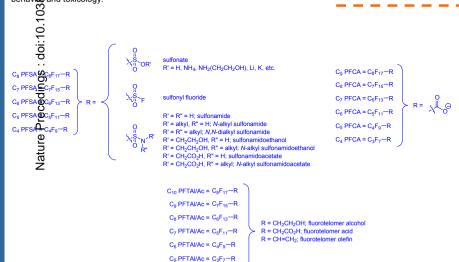
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Introduction

We intend uce a congener-specific numbering system for the C₄ through C₉ perfluor ated homologue groups of alkyl sulfonates, carboxylates, telomer alcohole and acids, and their derivatives. Increasing length of the carbon chain beyond leads to a corresponding rapid increase in the number of potential isomer Θ (C_4 =4, C_5 =8, C_6 =17, C_7 =39, and C_9 =89 congeners). There is a need for clear and unambiguous chemical shorthand to ensure accuracy and consistency in the future perfluorinated alkyl substance (PFA) literature, and to correct previous misconceptions that may have restricted research efforts into developing full-congener PFA analysis. If adopted by the research community. introduction of a numbering system at this relatively early stage of investigations into the congener-specific analysis, environmental behavior, and toxicol dv of PFAs would not require an arduous and difficult reassignment of historical structures and naming conventions presented in the prior art. Many PFA congeners are chiral (chiral centers denoted by a "*" in Figures 2 through 6), necessitating a consideration of their enantiospecific environmental behavion and toxicology

Table 1. Number of PFA congeners and stereoisomers in each of the C_3 through C_8 homologues.

Homologue group	# of congeners	# of chiral congeners	# with 1 chiral center	# with 2 chiral centers	# with 3 chiral centers	Total number of stereoisomers
3	2	0	-	-	-	-
4	4	1	1	-	-	2
5	8	3	3	-	-	6
6	17	9	8	1	-	20
7	39	24	19	5	-	58
8	89	66	48	17	1	172



 C_4 PFTAl/Ac = C_2F_5 -R

Figure 1. PFA structures for which the proposed numbering system applies.

Figure 2. Structures and numbering system for the C_4 perfluorinated chains.

	#	Substitution	Structure
C ₄	1	1,1'-dimethylethyl	CF ₃
	_	4 411	F ₃ C R CF ₃ CF ₃
	2	1-methylpropyl	F ₃ C * R
	ω	2-methylpropyl	F ₃ C F ₈
	4	n-butyl	F ₃ C F F R

Figure 3. Structures and numbering system for the C_5 perfluorinated chains.

	#	Substitution	Structure
C ₅	1	1-ethylpropyl	F ₃ C F ₂ CF ₃
	2	1,1'-dimethylpropyl	F ₃ C F ₃ R CF ₃
	3	1,2-dimethylpropyl	F ₃ C F ₃ R CF ₃
	4	2,2'-dimethylpropyl	F ₃ C CF ₃ F R CF ₃
	5	1-methylbutyl	F ₃ C F F R
	6	2-methylbutyl	F ₃ C F R
	7	3-methylbutyl	F ₃ C F F R
	8	n-pentyl	F ₃ C F F F F F F F F F F F F F F F F F F F

Substitution 2 1-ethyl-2-methylpropy 1,2,2'-trimethylpropyl 1-ethylbutyl 2-ethylbutyl 1,1'-dimethylbutyl 1,2-dimethylbutyl 2,2'-dimethylbutyl 2,3-dimethylbutyl 3,3'-dimethylbutyl 1-methylpentyl 2-methylpentyl

Figure 5. Structures and numbering system for the C_7 perfluorinated chains.

<u> </u>	#	Substitution	Structure		#	Substitution	Structure
C ₇	1	1,1'-diethylpropyl	CF₂CF₃ F	C ₇	22	2-ethylpentyl	F F F F
			F ₃ C R				F ₃ C
ᆫ			CF₂CF₃ F				F CF ₂ CF ₃
	2	1-ethyl-1',2-dimethylpropyl	CF ₂ CF ₃		23	3-ethylpentyl	CF ₂ CF ₃ F F F
			F ₃ C R				F ₉ C R
			CF ₃				F F
	3	1-ethyl-2,2'-dimethylpropyl	CF ₂ CF ₃		24	1,1'-dimethylpentyl	F CF ₃
			F ₃ C R				F ₃ C
			CF ₃				F CF3
	4	2-methyl-1-isopropylpropyl	C(CF ₃) ₂ F		25	1,2-dimethylpentyl	F CF ₃
			F ₃ C				F ₃ C * B
			CF ₂				* "
\vdash	5	1,1',2,2'-tetramethylpropyl	CF ₂	I	26	1,3-dimethylpentyl	CF ₃ CF ₃
		.,.,=,=,,,,,,,,,,,,,,,,,,,,,,,,,,	F ₂ C F ₃			.,,	F ₉ C、「↓ 「↓
			CF ₃				T F T F R
H	6	1-ethyl-1'-methylbutyl	F CF ₂ CF ₃	l	27	1,4-dimethylpentyl	F CF3
	ľ	1-ethyl-1-methylbutyl	1 5 1*		-	1,1 amnouny pointy.	F ₉ C. CF ₃
			F ₃ C R CF ₃				FFR
H	7	1-ethyl-2-methylbutyl	F CF ₂ CF ₃	l ⊢	28	2,2'-dimethylpentyl	F F
	ľ	1 culyi 2 mellyibatyi	↓ f ↓ t				F ₃ C F CF ₃
			F ₃ C R				Y F Y F R
L	8	1-ethyl-3-methylbutyl	CF ₃ CF ₂ CF ₃	l ⊢	29	2,3-dimethylpentyl	F CF ₃
	ľ	1-ettlyF5-mettlyDdtyf	↓ F ↓*		1-	2,0 amiomy pointy.	F ₃ C F CF ₃
			F ₃ C R				CF ₃ F
	9	2-ethyl-1-methylbutyl	F CF ₃	l ⊢	30	2,4-dimethylpentyl	F F
	0	2-ettlyr r-mettlyibatyr	11:		00	2,4 dimontyipontyi	F ₃ C CF ₃ CF ₃
			F ₃ C F R				Y I Y I R
_	10	2-ethyl-2'-methylbutyl	ĊF₂CF₃	l ⊢	31	3,3'-dimethylpentyl	F F
	10	2-ethyl-2-methylbutyl	CF ₃			o,o amnomy ponty.	F ₃ C F F
			F ₃ C R				CF ₃ F
			CF ₂ CF ₃	_	_		F F
	11	2-ethyl-3-methylbutyl	CF ₃ F		32	3,4-dimethylpentyl	CF ₃ F
			F ₃ C R				F ₃ C P
			F F CF ₂ CF ₃	l ∟			F F F F
	12	1,1',2-trimethylbutyl	F CF ₃ CF ₃		33	4,4'-dimethylpentyl	CF3 F
			F ₃ C R				F ₃ C R
			F30 + h				
			F [CF ₃	ı ∟	Ш		CF ₃ F
	13	1,1',3-trimethylbutyl	F [CF ₃		34	1-methylhexyl	CF ₃ F CF ₃
	13	1,1',3-trimethylbutyl	CF ₃ CF ₃		34	1-methylhexyl	F F CF ₂
			F CF ₃ CF ₃ CF ₃ F ₃ C F ₃ R F CF ₃				F F CF3
	13	1,1',3-trimethylbutyl	F CF3 F CF3 F CF3 F CF3		34	1-methylhexyl 2-methylhexyl	F F CF3
			F CF3 CF3 F				F F CF3
		1,2,2'-trimethylbutyl	F F CF3 CF3 CF3 F5C F5 F6 F5C F5 F7 F5C F5 F7 F5C F5			2-methylhexyl	F F F F F F F F F F F F F F F F F F F
			F CF3 CF3 CF3 CF3 CF3 F3C F3C F3C				F F F F F F F F F F F F F F F F F F F
	14	1,2,2'-trimethylbutyl	F F CF3 CF3 CF3 F5C F5 F6 F5C F5 F7 F5C F5 F7 F5C F5		35	2-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14	1,2,2'-trimethylbutyl	F CF3 CF3 CF3 F3C F3C F3C F3C F3C		35 36	2-methylhexyl 3-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14	1,2,2'-trimethylbutyl	F CF3 CF3 CF3 F3C F3C F3C F3C F3C		35	2-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₄ CF ₃ F ₅ C F ₅ CF ₃ F ₅ C F ₅ CF ₃ F ₅ C F ₅ CF ₅ CF ₃ CF ₅ CF ₅		35 36	2-methylhexyl 3-methylhexyl	F ₂ C F ₃ F ₄ F ₇
	14	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl	F ₁ CF ₃ CF ₃ CF ₃ CF ₃ CF ₃ F ₄ CF ₃ CF ₃ F ₅ CF ₃ F ₅ CF ₃		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl	F ₃ C F ₁ F ₂ F ₃ F ₃ F ₄ F ₅ F ₅ F ₇
	14	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₅ C F ₅ F ₅ C F ₅ F ₇ C F ₇ C F ₇ F ₇ C F ₇ C F ₇ F ₇ C F		35 36	2-methylhexyl 3-methylhexyl	F ₃ C F ₁ F ₂ F ₃ F ₃ F ₄ F ₅ F ₅ F ₇
	15	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₃ F ₅ C F ₃ F ₅ C F ₅ F ₅		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl	F F CF ₃ F ₃ C F F F F F F F F F F F F F F F F F F F
	15	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₃ F ₅ C F ₃ F ₅ C F ₅ F ₅		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F CF3 F CF3 F F F F F F F F F F F F F F F F F F F
	15	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl	F ₉ C F ₅ F ₇ C F ₅ F ₇ C F ₇		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl 2,2',3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₄ CF ₃ F ₅ C F ₅ F ₇ CF ₃ F ₅ C F ₅ F ₇ F ₇ CF ₃ CF ₃ F ₇		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F CF3 F CF3 F F F F F F F F F F F F F F F F F F F
	14 15 16 17	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl	F ₉ C		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16	1,2,2'-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3'-trimethylbutyl 2,2',3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₄ CF ₃ F ₅ C F ₅ F ₇ CF ₃ F ₅ C F ₅ F ₇ F ₇ CF ₃ CF ₃ F ₇		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16 17	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl	F ₉ C		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16 17 18	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl 2,3,3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₄ CF ₃ F ₅ C F ₅ F ₇ CF ₃ F ₅ C F ₅ F ₇ F ₇ CF ₃ F ₅ C F ₅ F ₇		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16 17	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl	F ₉ C F ₃ F ₅ C F ₃ C		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16 17 18	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl 2,3,3-trimethylbutyl	F ₃ C F ₃ CF ₃ F ₃ C F ₄ CF ₃ F ₅ C F ₅ F ₇ CF ₃ F ₅ C F ₅ F ₇ F ₇ CF ₃ F ₅ C F ₅ F ₇		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F
	14 15 16 17 18	1,2,2-trimethylbutyl 1,2,3-trimethylbutyl 1,3,3-trimethylbutyl 2,2',3-trimethylbutyl 2,3,3-trimethylbutyl	F ₉ C F ₉ CF ₉ F ₉ C F ₉ CF ₉ F ₉ C F ₉ F ₉ C F ₉ F ₉ F ₉ C F ₉		35 36 37	2-methylhexyl 3-methylhexyl 4-methylhexyl 5-methylhexyl	F F F F F F F F F F F F F F F F F F F

	# Substitution	Structure	1 -	#	Substitution	Structure		#	Substitution	Structure	_	#	Substitution	Structure
C ₈	1 1-ethyl-1',2,2'-trimethylpropyl	CF ₂ CF ₃	C ₈	22	2-ethyl-3,3'-dimethylbutyl	CF ₃ CF ₂ CF ₃	C ₈	43	3-ethyl-3'-methylpentyl	GF ₂ GF ₃ F	C ₈	64	1-ethylhexyl	F F CF2CF3
		F ₃ C R CF ₃				F ₃ C CF ₃ F R				F ₃ C CF ₃ F R				F ₃ C F F F F
	2 1-ethyl-1'-isopropylpropyl	F ₃ C F ₂ CF ₃		23	1,1',2,2'-tetramethylbutyl	F ₃ C F ₃ CF ₃ R CF ₃ CF ₃		44	3-ethyl-4-methylpentyl	F ₃ C F ₂ CF ₃ F F F F F		65	2-ethylhexyl	F_3C F
	3 1-isopropropyl-1',2-dimethylpropyl	F ₃ C CF ₃ R C(CF ₃) ₂ F		24	1,1',2,3-tetramethylbutyl	F CF ₃ R CF ₃ CF ₃		45	1-isopropylpentyl	F ₃ C F F R		66	3-ethylhexyl	F CF ₂ CF ₃ F F F F F
	4 1-isopropyl-2,2'-dimethylpropyl	F ₃ C F ₃ R C(CF ₃) ₂ F		25	1,1',3,3'-tetramethylbutyl	CF ₃ CF ₃ F		46	2-isopropylpentyl	F ₃ C F F F R R F C(CF ₃) ₂ F		67	4-ethylhexyl	F F F F F F F F F F F F F F F F F F F
XUC	5 1- <i>tert</i> -butyl-butyl	F ₃ C F F R		26	1,2,2',3-tetramethylbutyl	F ₃ C CF ₃ R CF ₃ CF ₃		47	1,1',2-trimethylpentyl	F ₃ C F F CF ₃ R CF ₃		68	1,1'-dimethylhexyl	F ₃ C F F CF ₃ R CF ₃
Cuil	1,1'-diethylbutyl	F CF2CF3 F CF2CF3		27	1,2,3,3'-tetramethylbutyl	CF ₃ F GF ₃ R CF ₃ CF ₃		48	1,1',3-trimethylpentyl	CF ₃ CF ₃		69	1,2-dimethylhexyl	F F CF3
8		F CF ₂ CF ₃		28	2,2',3,3'-tetramethylbutyl	CF ₃ F CF ₃ F R CF ₃ F R		49	1,1',4-trimethylpentyl	F ₃ C F F CF ₃ R CF ₃ F CF ₃		70	1,3-dimethylhexyl	F CF ₃ CF ₃
DOG		F ₃ C F ₂ CF ₃ F _R CF ₂ CF ₃		29	2,2',4,4'-tetramethylbutyl	F(F ₃ C) ₂ C F CF ₃ R		50	1,2,2'-trimethylpentyl	F ₃ C F ₃ CF ₃ R		71	1,4-dimethylhexyl	F F CF ₃ F F F R CF ₃
957 1		F ₃ C F C(CF ₃) ₂ F		30	1-propyl-1'-methylbutyl	F (CF ₂) ₂ CF ₃ F CF ₃		51	1,2,3-trimethylpentyl	F ₃ C F ₃ CF ₃ R F CF ₃ CF ₃		72	1,5-dimethylhexyl	F ₃ C F F F R F F F F F F F F F F F F F F F
900	0 1-isopropyl-2-methylbutyl	F ₃ C F R C(CF ₃) ₂ F		31	1-propyl-2-methylbutyl	F (CF ₂) ₂ CF ₃ F * R CF ₃		52	1,2,4-trimethylpentyl	F ₃ C F F CF ₃ R CF ₃ CF ₃		73	2,2'-dimethylhexyl	F_3C F
/nore	1 1-isopropyl-3-methylbutyl	F ₃ C CF ₃ F R		32	1-propyl-3-methylbutyl	F ₃ C CF ₃ F R		53	1,3,3'-trimethylpentyl	F ₃ C F ₃ F R F F F F		74	2,3-dimethylhexyl	F ₃ C F _F F _F CF ₃ R _F R
1038/1	: I	F ₃ C CF ₃ F R		33	1-ethyl-1'-methylpentyl	F ₃ C F F CF ₂ CF ₃		54	1,3,4-trimethylpentyl	F ₃ C F ₃ F R F R		75	2,4-dimethylhexyl	F ₃ C F ₈
40i.40		F ₃ C F CF ₂ CF ₃		34	1-ethyl-2-methylpentyl	F ₃ C F F CF ₂ CF ₃		55	1,4,4'-trimethylpentyl	F ₃ C CF ₃ F R R CF ₃ F R		76	2,5-dimethylhexyl	F ₃ C CF ₃ F F F
. 500		F ₃ C F ₂ CF ₃		35	1-ethyl-3-methylpentyl	F ₃ C F ₃ F R F ₃ CF ₃ F		56	2,2',3-trimethylpentyl	F ₃ C F ₃ F ₄ CF ₃ F ₅ F ₇			3,3'-dimethylhexyl	F ₃ C F CF ₃ F R
		F CF ₂ CF ₃ F CF ₃ R F CF ₃		36	1-ethyl-4-methylpentyl	F ₃ C F F F F F		57	2,3,3'-trimethylpentyl	F ₃ C CF ₃ F R		78	3,4-dimethylhexyl	F ₃ C F ₃ F ₅ F ₇ R
a d		F CF ₂ CF ₃ F R		37	2-ethyl-1-methylpentyl	F ₃ C F F R R F CF ₂ CF ₃		58	2,3,4-trimethylpentyl	F ₃ C CF ₃ CF ₃ R		79	3,5-dimethylhexyl	F ₃ C CF ₃ F F R
7		CF ₃ CF ₂ CF ₃ F * R CF ₃ F * R		38	2-ethyl-2-methylpentyl	F ₃ C F CF ₃ R F CF ₂ CF ₃		59	2,4,4'-trimethylpentyl	F ₃ C CF ₃ F R F R			4,4'-dimethylhexyl	F ₃ C F ₃ F R
	8 2-ethyl-1,1'-dimethylbutyl	F ₃ C F ₂ CF ₃ CF ₃ CF ₃ CF ₃		39	2-ethyl-3-methylpentyl	CF ₃ F F R F GF ₂ CF ₃		60	3,3',4-trimethylpentyl	F ₃ C CF ₃ F R		81	4,5-dimethylhexyl	F ₃ C CF ₃ F F R
	9 2-ethyl-1,2'-dimethylbutyl	F ₃ C F CF ₂ CF ₃ F CF ₃ CF ₃		40	2-ethyl-4-methylpentyl	F ₃ C F ₃ F R F CF ₂ CF ₃		61	3,4,4'-trimethylpentyl	F ₃ C CF ₃ F R CF ₃ F R			5,5'-dimethylhexyl	F ₃ C CF ₃ F F F R
	0 2-ethyl-1,3-dimethylbutyl	F ₃ C CF ₂ CF ₃ F CF ₃ CF ₃		41	3-ethyl-1-methylpentyl	CF2CF3 F F3C F F CF3		62	1-propylpentyl	F ₃ C F F (CF ₂) ₂ CF ₃		83	1-methylheptyl	F ₃ C F _F F F CF ₃
	1 2-ethyl-2',3-dimethyl-butyl	F ₃ C CF ₃ F _R CF ₃ F _R		42	3-ethyl-2-methylpentyl	F ₃ C F F R F CF ₃		63	2-propylpentyl	F ₃ C F F R R F (CF ₂) ₂ CF ₃		84	2-methylheptyl	F_3C F

٠.			
	85	3-methylheptyl	F ₃ C F F F F F R
1	86	4-methylheptyl	F_3C F
1	87	5-methylheptyl	F ₃ C F F F F F F F F F F F F F F F F F F F
1	88	6-methylheptyl	F ₃ C F F F F R
1	89	n-octyl	F ₃ C F F F F F F F F F F F F F F F F F F F

Figure 6. Structures and numbering system for the C_8 perfluorinated chains.

Conclusion

The proposed numbering system for PFAs presented herein offers a concise and unambiguous means for communicating molecular structures of these important contaminants within the scientific literature. In addition, the system outlines the number and range of possible structures that may be present in environmental and biological systems, and for which more comprehensive congener-specific analysis and testing methods should be developed.

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