1 <u>**Supplemental Information**</u>

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3 Yields of Perfluorocarboxylic Acids from the 4 Atmospheric Oxidation of Montreal Protocol 5 Related Gases

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SI 1 CF$_3$C(O)H, C$_2$F$_5$C(O)H and C$_3$F$_7$C(O)H Quantum Yields, UV Spectra and Lifetimes with Respect to Photolysis.

SI 1.1 CF$_3$C(O)H quantum yields used for TUV models
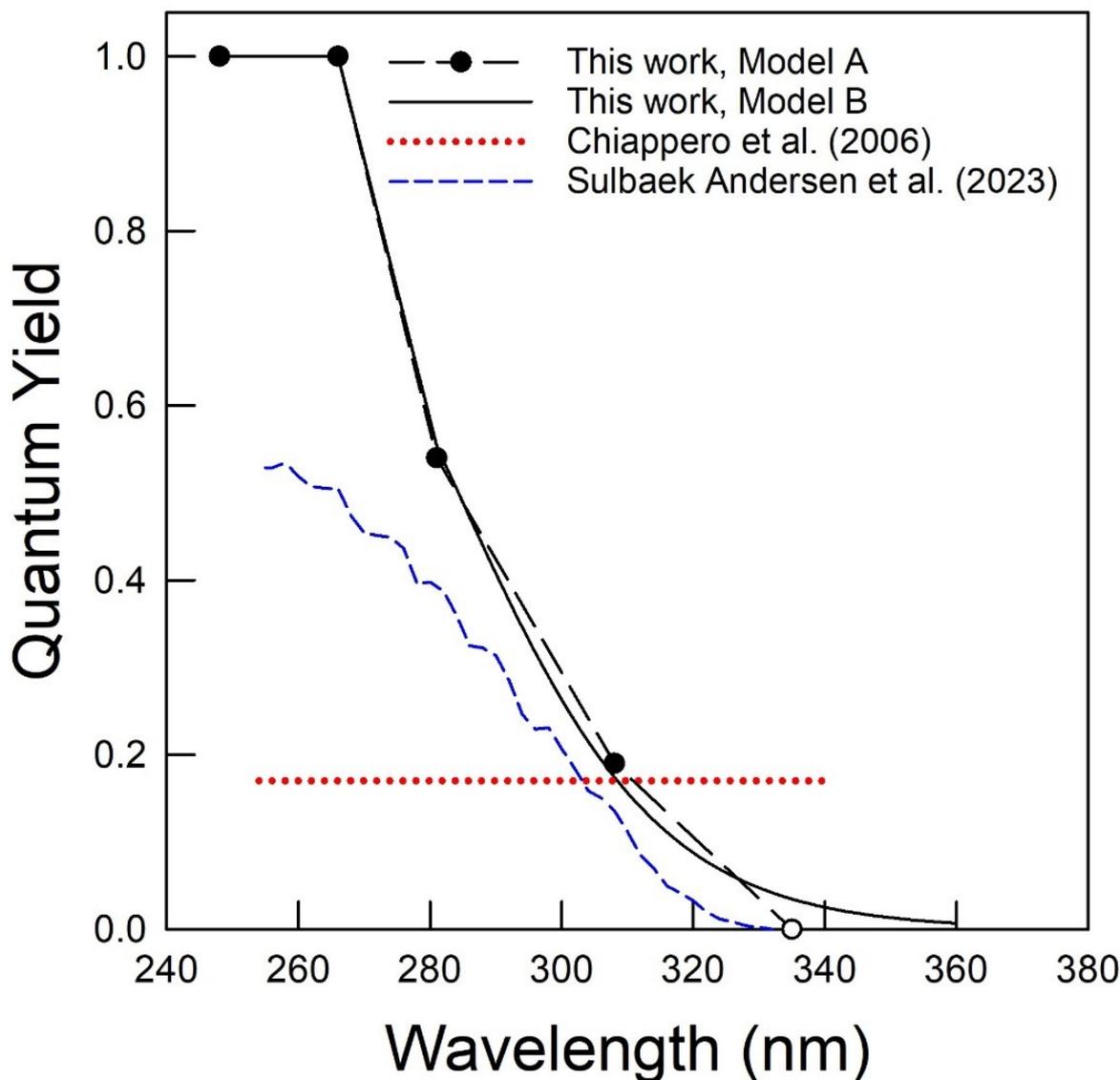
**SI Figure 1.1** Quantum yields used by Chiappero *et al.*[1] (red dotted trace), Sulbaek Andersen *et al.*[2] (blue dashed trace), This work - Model A (circles and dashed black trace) and This work – Model B (solid black trace) for estimating atmospheric lifetime of CF$_3$C(O)H with respect to photolysis. No pressure dependence was assumed in the work by Chiappero *et al.* and Sulbaek Andersen *et al.* The quantum yield trace shown for the present work is for 1 atmosphere pressure (a Stern-Volmer dependence with quantum yield equal to 1 at 0 Torr pressure was used in the Tropospheric Ultraviolet and Visible (TUV) Radiation Models A and B).
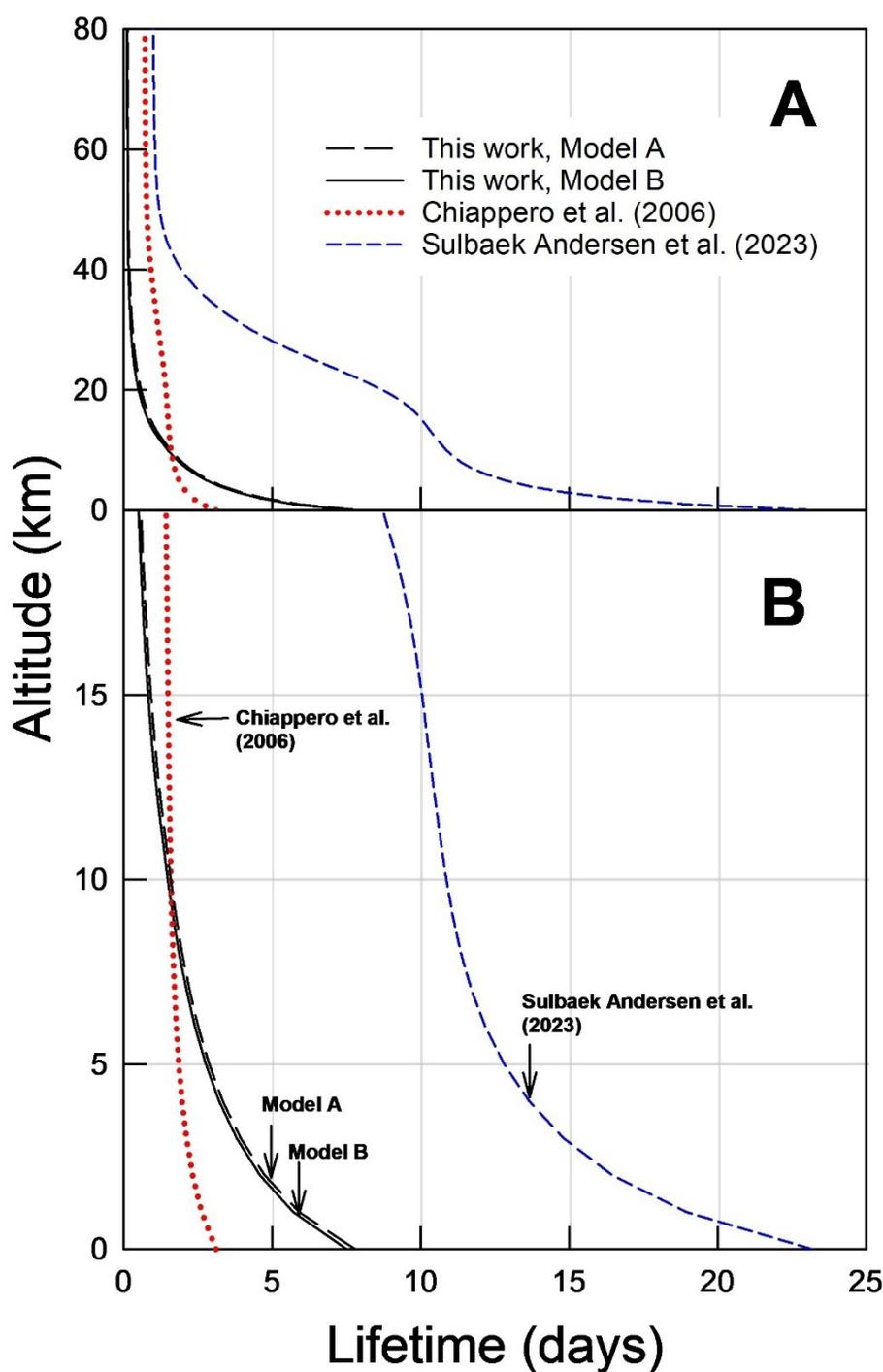
SI 1.2   CF$_3$C(O)H Lifetimes

SI Figure SI 1.2 Traces for the average atmospheric lifetimes for CF$_3$C(O)H (average of atmospheric lifetimes for Equator and 40°N, 21st March) with respect to photolysis determined from the photolysis frequency data produced by the Tropospheric Ultraviolet and Visible (TUV) Radiation model runs (see main text for details). Panel A shows the average atmospheric lifetime versus altitude from 0 km through 80 km altitude. Panel B show a truncate display of the data in Panel A, limited to the troposphere-tropopause region. The data shown are for the quantum yield data used by Chiappero et al.[1] (red dotted trace), Sulbaek Andersen et al.[2] (blue dashed trace), this work – Model A (dashed black trace) and Model B (solid black trace). Pressure dependences were included for the Model A and B input data.
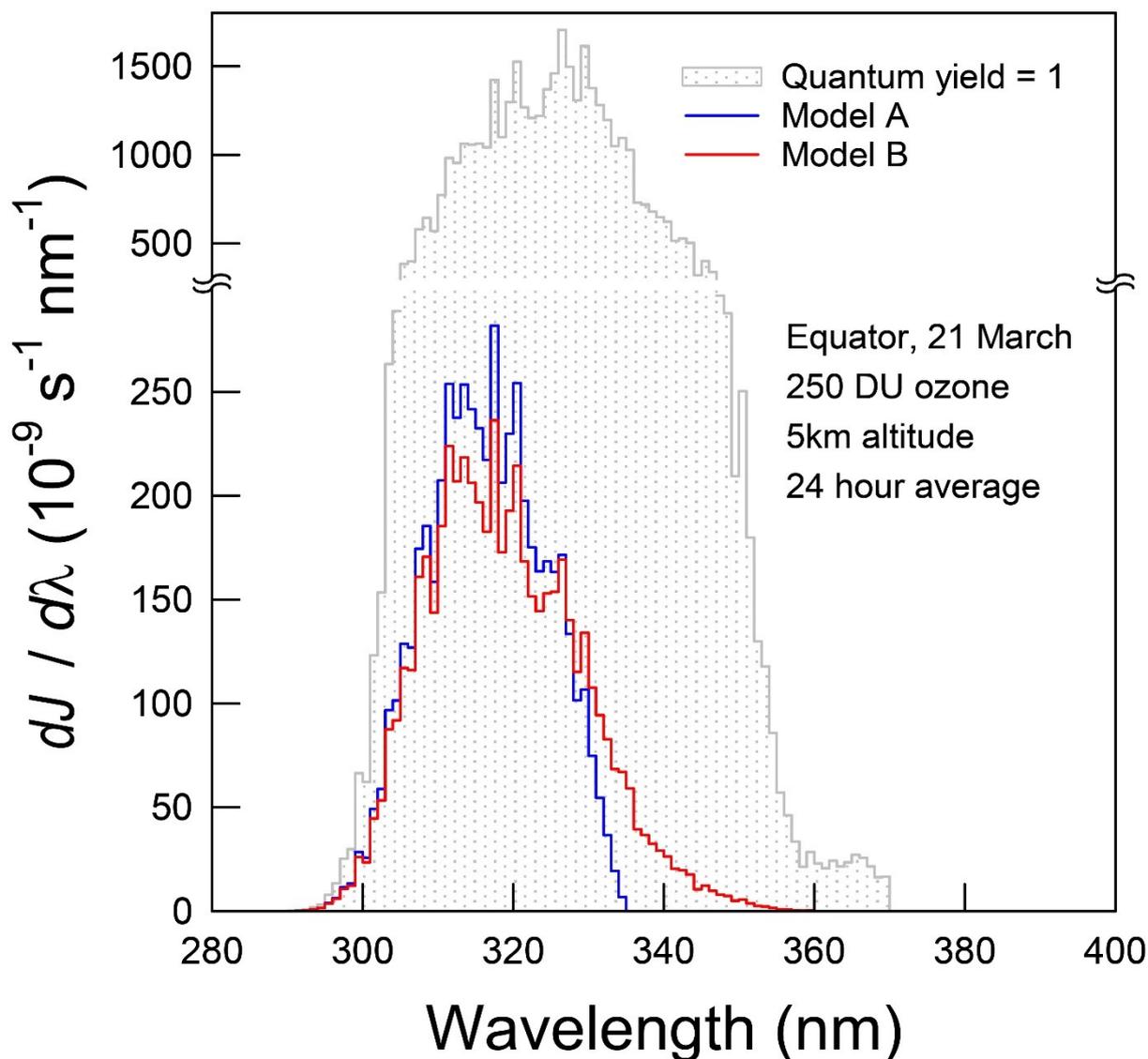
66
67 **SI Figure SI 1.3** Derivatives for the photolysis frequency with respect to wavelength versus
68 wavelength using two different quantum yield models (Model A and B, see text), computed at 1
69 nm resolution with the TUV model for the conditions indicated. Photolysis frequencies are the
70 area under the respective curves. A Stern-Volmer pressure dependence was applied at each
71 wavelength. For reference, the spectral contribution to absorption only (i.e., quantum yield =1)
72 is also shown; note change in vertical scale.
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SI 1.4   TUV Model Data Input

SI Table 1.4.1 UV Spectra used in the present work, at 298 K (no temperature dependence).
Note different resolutions: $CF_3C(O)H$ (1 nm), $C_2F_5C(O)H$ (5 nm), and $C_3F_7C(O)H$ (5 nm).

Wavelength (nm)	Cross (Section $\times 10^{-20}$ (cm^2)		
	CF$_3$C(O)H*	C$_2$F$_5$C(O)H**	C$_3$F$_7$C(O)H***
200			0.34
205			0.12
210	0.197		0.21
211	0.192		
212	0.179		
213	0.172		
214	0.159		
215	0.152		0.16
216	0.14		
217	0.132		
218	0.121		
219	0.113		
220	0.105		0.11
221	0.098		
222	0.09		
223	0.084		
224	0.08		
225	0.076		0.14
226	0.074		
227	0.073		
228	0.075		
229	0.075		
230	0.078	0.15	0.09
231	0.081		
232	0.086		
233	0.091		
234	0.097		
235	0.104	0.15	0.1
236	0.112		
237	0.121		
238	0.131		
239	0.142		
240	0.155	0.21	0.15
241	0.169		
242	0.184		
243	0.201		
244	0.22		
245	0.24	0.29	0.24
246	0.262		

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247	0.285		
248	0.311		
249	0.339		
250	0.369	0.4	0.41
251	0.4		
252	0.433		
253	0.472		
254	0.511		
255	0.548	0.6	0.68
256	0.591		
257	0.638		
258	0.686		
259	0.737		
260	0.789	0.89	1.03
261	0.84		
262	0.896		
263	0.954		
264	1.02		
265	1.09	1.26	1.54
266	1.15		
267	1.22		
268	1.29		
269	1.35		
270	1.42	1.75	2.18
271	1.5		
272	1.58		
273	1.66		
274	1.74		
275	1.82	2.34	2.97
276	1.89		
277	1.96		
278	2.03		
279	2.11		
280	2.19	2.99	3.87
281	2.28		
282	2.35		
283	2.42		
284	2.5		
285	2.57	3.68	4.87
286	2.63		
287	2.67		
288	2.73		
289	2.79		
290	2.86	4.36	5.83
291	2.92		
292	2.94		

293	3		
294	3.05		
295	3.06	4.97	6.79
296	3.08		
297	3.08		
298	3.1		
299	3.14		
300	3.17	5.41	7.45
301	3.2		
302	3.15		
303	3.12		
304	3.15		
305	3.13	5.64	7.97
306	3.07		
307	3.03		
308	2.97		
309	2.95		
310	2.92	5.78	8.29
311	2.92		
312	2.91		
313	2.78		
314	2.67		
315	2.65	5.38	7.77
316	2.62		
317	2.52		
318	2.42		
319	2.33		
320	2.25	5.36	7.83
321	2.19		
322	2.13		
323	2.08		
324	2.06		
325	1.9	4.47	6.4
326	1.72		
327	1.64		
328	1.62		
329	1.55		
330	1.44	3.64	5.32
331	1.35		
332	1.26		
333	1.18		
334	1.13		
335	1.06	3.16	4.74
336	1.01		
337	0.993		
338	0.891		

339	0.73		
340	0.622	2.01	2.91
341	0.585		
342	0.569		
343	0.531		
344	0.471		
345	0.425	1.37	1.98
346	0.385		
347	0.337		
348	0.31		
349	0.286		
350	0.246	1.05	1.52
351	0.235		
352	0.232		
353	0.162		
354	0.096		
355	0.071	0.44	0.65
356	0.058		
357	0.05		
358	0.044		
359	0.042		
360	0.038	0.14	0.13
365		0.08	0.04
370		0.07	0
375		0.05	

* From JPL Publicationn 19-5, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 19, National Aeronautics and Space Administration Jet Propulsion Laboratory California Institute of Technology Pasadena, California, May 2020.

** From IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr. This datasheet last evaluated: June 2015; last change in preferred values: June 2014.

*** From IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr. This datasheet last evaluated: June 2015; last change in preferred values: June 2010.

SI Table 1.4.2 Quantum yields used the present work, 298 K, 1 atmosphere of pressure (a Stern-Volmer pressure dependence with quantum yield equal to 1 at 0 Torr pressure was used in the models). Note, the quantum yields for $C_2F_5C(O)H$ and $C_3F_7C(O)H$ are equal to those of $CF_3C(O)H$ with a 10 nm offset.

	Quantum yields	
Wavelength (nm)	**$CF_3C(O)H$**	**$C_2F_5C(O)H$ & $C_3F_7C(O)H$**
248	1.000	1
266	1.000	1
281	0.554	
282	0.538	
283	0.521	
284	0.505	
285	0.488	

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286	0.472	
287	0.456	
288	0.440	
289	0.423	
290	0.408	
291	0.392	0.554
292	0.376	0.538
293	0.361	0.521
294	0.346	0.505
295	0.331	0.488
296	0.317	0.472
297	0.303	0.456
298	0.289	0.440
299	0.276	0.423
300	0.263	0.408
301	0.250	0.392
302	0.238	0.376
303	0.227	0.361
304	0.215	0.346
305	0.204	0.331
306	0.194	0.317
307	0.184	0.303
308	0.174	0.289
309	0.165	0.276
310	0.156	0.263
311	0.148	0.250
312	0.140	0.238
313	0.132	0.227
314	0.125	0.215
315	0.118	0.204
316	0.111	0.194
317	0.105	0.184
318	0.099	0.174
319	0.093	0.165
320	0.088	0.156
321	0.083	0.148
322	0.078	0.140
323	0.073	0.132
324	0.069	0.125
325	0.065	0.118
326	0.061	0.111
327	0.057	0.105
328	0.054	0.099
329	0.051	0.093
330	0.047	0.088
331	0.045	0.083
332	0.042	0.078
333	0.039	0.073

334	0.037	0.069
335	0.035	0.065
336	0.033	0.061
337	0.031	0.057
338	0.029	0.054
339	0.027	0.051
340	0.025	0.047
341	0.024	0.045
342	0.022	0.042
343	0.021	0.039
344	0.019	0.037
345	0.018	0.035
346	0.017	0.033
347	0.016	0.031
348	0.015	0.029
349	0.014	0.027
350	0.013	0.025
351	0.012	0.024
352	0.012	0.022
353	0.011	0.021
354	0.010	0.019
355	0.010	0.018
356	0.009	0.017
357	0.008	0.016
358	0.008	0.015
359	0.007	0.014
360	0.007	0.013
361		0.012
362		0.012
363		0.011
364		0.010
365		0.010
366		0.009
367		0.008
368		0.008
369		0.007
370		0.007

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SI 2 Estimated perfluorocarboxylic acid yields from compounds listed in Table 2.

In the following evaluations of the compound-specific yields of PFCAs, the overall yields are obtained as the sum of the individual contributions from the yields of primary degradation products and/or radical intermediates multiplied by their evaluated yields of PFCAs (see Table 1 in the main text).

SI 2.1 CFCs

SI 2.1.1 CFC-113a (CCl_3CF_3), < 10 % TFA

The sole atmospheric fate of CCl_3CF_3 is photolysis in the stratosphere. Further atmospheric degradation leads to CF_3CCl_2O alkoxy radicals. CF_3CCl_2O is converted to $CF_3C(O)Cl$ through Cl elimination.[3-5] The stratospheric photolytic lifetime for $CF_3C(O)Cl$ is approximately 16 days[6] and uptake and hydrolysis in cloud water in the troposphere (and conversion to TFA) will therefore be unimportant. Photolysis of $CF_3C(O)Cl$ proceeds via multiple channels, one of which gives $CF_3C(O)$ radicals, which, if stabilized, have the potential to yield TFA, through the reaction with O_2 and subsequent reaction of the acyl peroxy radical with HO_2. The latter reaction occurs in competition with reaction with NO which reduces the maximum possible yield (39 ± 4 %, at room temperature) of TFA from the HO_2 reaction with $CF_3C(O)O_2$.[7] The quantum yield of $CF_3C(O)$ radicals in the photolysis of $CF_3C(O)Cl$ under stratospheric conditions is unclear. The global average concentration of HO_2 in the stratosphere is low in comparison to NO, and the yield of TFA in the atmospheric degradation of CCl_3CF_3 is expected to be < 10 %. Without a detailed atmospheric chemistry and transport model study, a more quantitative assessment of the yield of TFA is not possible.

SI 2.1.2 CFC-114a (CCl_2FCF_3), ≈ 10 % TFA

The sole fate of CCl_2FCF_3 is photolysis in the stratosphere, yielding CF_3CFCl radicals, that will form the corresponding alkoxy radical CF_3CFClO. The dominant, if not sole, fate of CF_3CFClO is decomposition to give $CF_3C(O)F$ and Cl.[4, 8] The tropospheric fate of $CF_3C(O)F$ is incorporation into clouds followed by hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] In the stratosphere photolysis is the major (≈ 90 %) fate of $CF_3C(O)F$, the remaining ≈ 10 % is transported to the troposphere.[10] The yield of TFA in the atmospheric degradation of CF_3CHFCl is expected to be ≈ 10 %.

SI 2.1.3 CFC-216ba ($CClF_2CClFCF_3$), ≈ 10 % TFA

The sole fate of $CClF_2CClFCF_3$ is photolysis in the stratosphere, yielding $CF_2CClFCF_3$ and $CClF_2CFCF_3$ radicals, that will form the corresponding alkoxy radicals $C(O)F_2CClFCF_3$ or $CClF_2C(O)FCF_3$. The former will decompose to COF_2 and $CClFCF_3$ radicals that will eventually end up as CF_3CFClO radicals. The dominant, if not sole, fate of CF_3CFClO is decomposition to give $CF_3C(O)F$ and Cl.[4, 8] The tropospheric fate of $CF_3C(O)F$ is incorporation into water droplets followed by hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] The main (≈ 90 %) stratospheric fate of $CF_3C(O)F$ is photolysis.[10] $CClF_2C(O)FCF_3$ radicals will decompose to $CClF_2C(O)F$ and CF_3 radicals, neither of which can

undergo reaction to form TFA. The yield of TFA in the atmospheric degradation of $CClF_2CClFCF_3$ is expected to be $\approx 10\ \%$.

SI 2.2   HCFCs/Halons

SI 2.2.1   HCFC-124 (CF_3CHFCl), 100 % TFA

The main atmospheric fate of CF_3CHFCl is reaction with OH radicals in the troposphere. Atmospheric degradation of CF_3CHFCl leads to CF_3CFClO alkoxy radicals. The dominant, if not sole, fate of CF_3CFClO is decomposition to give $CF_3C(O)F$ and Cl.[4, 8] The tropospheric fate of $CF_3C(O)F$ is incorporation into water droplets followed by hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] The yield of TFA in the atmospheric degradation of CF_3CHFCl is expected to be 100%.

SI 2.2.2   HCFC-133a (CF_3CH_2Cl), < 62 % TFA

The main atmospheric fate of CF_3CH_2Cl is reaction with OH radicals in the troposphere. The degradation initiated by OH radicals results in the formation of CF_3CHClO alkoxy radicals. The atmospheric fate of CF_3CHClO is decomposition and reaction with O_2.[11] Reaction with O_2 gives $CF_3C(O)Cl$ and HO_2, while decomposition will proceed through three channels:

$$CF_3CHClO + M \rightarrow CF_3 + HC(O)Cl + M \qquad (1)$$

$$CF_3CHClO + M \rightarrow CF_3CO + HCl + M \qquad (2)$$

$$CF_3CHClO + M \rightarrow CF_3C(O)H + Cl + M \qquad (3)$$

At ground level and at room temperature, decomposition and reaction with O_2 are of almost equal importance, i.e., the yield of $CF_3C(O)Cl$ is 52%.[11] At higher altitudes, the importance of reaction with O_2 will increase. If CH_3CHClO is formed through reaction of CF_3CHClO_2 radicals with NO this can result in chemical activation of the resulting CF_3CHClO radicals, and in turn lead to enhanced decomposition.

The O_2 reaction channel product, $CF_3C(O)Cl$, undergoes photolysis in competition with incorporation into water droplets. The estimated tropospheric photolytic lifetime for $CF_3C(O)Cl$ for an overhead sun is 23 days.[12] The atmospheric lifetime of $CF_3C(O)Cl$ with respect to uptake and hydrolysis in cloud water is 5–30 days.[9] It has been estimated that, on average, 60 % of $CF_3C(O)Cl$ is converted into TFA.[3] Further reactions of CF_3CHClO decomposition products from reaction 2 and 3, CF_3CO and $CF_3C(O)H$, have the potential to yield TFA.

$CF_3C(O)H$ can undergo photolysis, reaction with OH radicals, and wet/dry deposition in the atmosphere. Reaction of HO_2 radicals have been recently proposed as a sink for $CF_3C(O)H$, but this reaction has yet to be observed experimentally. Current understanding of the atmospheric fate of $CF_3C(O)H$ suggests that its atmospheric fate is dominated by destruction by photolysis (average photolytic lifetime in the troposphere of 3 days (this work)) and wet/dry deposition (lower limit of 2 days). Photolysis of $CF_3C(O)H$ leads to CF_3 and $C(O)H$ radicals which cannot contribute to the formation of TFA.[13]

The rate of reaction of $CF_3C(O)H$ with OH radicals is slow with a moderate dependence on temperature. The tropospheric lifetime (at 272 K) is estimated to be 23 days, increasing to 30 days between 8 and 11 km altitude,[14] and thus of less importance in the fate of $CF_3C(O)H$. Oxidation of $CF_3C(O)H$ initiated by OH radicals will produce CF_3CO radicals, which undergo reaction with O_2 to yield

acylperoxy radicals, $CF_3C(O)O_2$. These acylperoxy radicals can react with HO_2, NO, or NO_2. Reaction of $CF_3C(O)O_2$ with HO_2 radicals gives TFA in a 39 % yield.[7] Reaction with HO_2 radicals occurs in competition with reaction with NO which significantly reduces the maximum possible yield (39 ± 4 %, at room temperature) of TFA from the HO_2 reaction with $CF_3C(O)O_2$. The importance of formation of TFA from $CF_3C(O)O_2$ depends on the local environment and the atmospheric abundance ratio of NO to HO_2. The effective yield of TFA from $CF_3C(O)$ in the troposphere was indirectly accessed by Sulbaek Andersen *et al.*[15] in a global modelling study of emissions of HCFO-1233(zd). In their work, the atmospheric lifetimes for $CF_3C(O)H$ were 2 days and 20 days with respect to photolysis and reaction with OH radicals, respectively. With an overall yield of TFA of 2 %, the model results of Sulbaek Andersen *et al.* suggest that the molar yield of TFA in the reaction of OH radicals with $CF_3C(O)H$ (equivalent to considering the yield of TFA from $CF_3C(O)$), is on the order of $\sim$ 20 %.

Finally, on contact with liquid water, $CF_3C(O)H$ can produce aldehyde hydrates (gem-diols). These can, at least in the gas-phase, react with OH radicals (lifetime of approximately 90 days) and generate TFA in a yield of 100 %.[16] The overall impact of $CF_3C(O)H$ hydrate formation, in-cloud processing and wet/dry deposition of $CF_3C(O)H$ remains highly uncertain,[16, 17] hampered by the lack of quantitative characterization of the processes involved, e.g., Henry's law constant and hydration equilibrium constant for $CF_3C(O)H$. Assuming that the deposition lifetime for $CF_3C(O)H$ is 2 days (lower limit for a species such as HNO_3 which deposit without surface resistance)[18] and that hydration is efficient and converts $CF_3C(O)H$ into TFA with a yield of unity, then a maximum TFA yield of approximately 57 % can be expected from hydrate formation (see the main text for further discussion). Thus, based on an average atmospheric lifetime of 3 days with respect to photolysis, 23 days with respect to reaction with OH radicals, and 2 days with respect to deposition/hydrate formation, the upper limit for the TFA yield from $CF_3C(O)H$ is estimated at $\leq$ 58 %.

In reaction 2 above, the acyl radical, CF_3CO, can also lead to formation of TFA, though the reaction with O_2 and subsequent reaction of the acyl peroxy acyl radical with HO_2, as described above.

Based on the discussion above regarding the fate of $CF_3C(O)Cl$, the yield of TFA from hydrolysis of $CF_3C(O)Cl$ can be calculated as $0.52 \times (60$ %$) = 31$ %. An uncertainty of ± 10 % is estimated for this yield. Additional contributions from the atmospheric processing of $CF_3C(O)H$ or CF_3CO could be as much as $0.48 \times (\leq 58$ %$)$, i.e., ≤ 28%. Hence, the upper limit to the yield of TFA in the atmospheric degradation of CF_3CH_2Cl is 31% + 28% = 59 %. Without a detailed atmospheric chemistry and transport model study, a more quantitative assessment of the yield of TFA is not possible.

SI 2.2.3   **HCFC-225ca ($CF_3CF_2CHCl_2$), < 10 % TFA**

The atmospheric fate of $CF_3CF_2CHCl_2$ is reaction with OH radicals. Reaction with OH produces an alkyl radical that reacts with O_2 to give the peroxy radical $CF_3CF_2CCl_2O_2$. The peroxy radical reacts with NO to yield the alkoxy radical $CF_3CF_2CCl_2O$ which decomposes to give $COCl_2$ and CF_3CF_2 radicals. CF_3CF_2 will react with O_2 and NO to give CF_3CF_2O radicals. Ellis *et al.*[19] suggested a mechanism in which perfluoroalkyl peroxy radicals such as $CF_3CF_2O_2$ can react with α-hydrogen containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give CF_3CF_2OH in small amounts (1–10 %).[20] By analogy to the behaviour of other perhaloalcohols, CF_3CF_2OH will eliminate HF to give $CF_3C(O)F$.[21,22] The

245 tropospheric fate of $CF_3C(O)F$ is incorporation into water droplets followed by
246 hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] Thus, the yield of
247 TFA in the atmospheric degradation of $CF_3CF_2CHCl_2$ is expected to be < 10 %.

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249 **SI 2.2.4** **HCFC-233fb ($CCl_2FCH_2CF_3$), < 58 % TFA**

250 The atmospheric fate of $CH_2ClCH_2CF_3$ is reaction with OH radicals,
251 followed by reaction with O_2 and RO_2/NO to give $CCl_2FCH(O)CF_3$ radicals.
252 $CCl_2FCH(O)CF_3$ will decompose to give $CF_3C(O)H$ and CCl_2F radicals. As
253 discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can lead to
254 formation of TFA. Thus, the TFA yield from atmospheric processing of
255 $CCl_2FCH_2CF_3$ is estimated at < 58 %.

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257 **SI 2.2.5** **HCFC-243fa ($CHCl_2CH_2CF_3$), < 58 % TFA**

258 The atmospheric fate of $CHCl_2CH_2CF_3$ is reaction with OH radicals.
259 followed by reaction with O_2 and RO_2/NO to give $OCCl_2CH_2CF_3$ or
260 $CHCl_2CH(O)CF_3$ radicals. $OCCl_2CH_2CF_3$ will decompose to $COCl_2$ and CF_3CH_2
261 radicals. The latter will undergo further oxidation to give $CF_3C(O)H$.
262 $CHCl_2CH(O)CF_3$ will decompose to give $CF_3C(O)H$ and $CHCl_2$ radicals.
263 Independent of reaction site for the initial OH mediated abstraction of a hydrogen
264 atom, the subsequent reactions will lead to formation of $CF_3C(O)H$ in a yield of
265 100 %. As discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can
266 lead to formation of TFA. Thus, the TFA yield from processing of $CHCl_2CH_2CF_3$
267 is estimated at < 58 %.

268

269 **SI 2.2.6** **HCFC-244fa ($CHFClCH_2CF_3$), < 58 % TFA**

270 The atmospheric fate of $CHFClCH_2CF_3$ is reaction with OH radicals,
271 followed by reaction with O_2 and RO_2/NO to give $OCFClCH_2CF_3$ or
272 $CHFClCH(O)CF_3$ radicals. $OCFClCH_2CF_3$ will decompose to CFClO and CF_3CH_2
273 radicals. The latter will undergo further oxidation to give $CF_3C(O)H$.
274 $CHFClCH(O)CF_3$ will decompose to give $CF_3C(O)H$ and CHFCl radicals.
275 Independent of reaction site for the initial OH mediated abstraction of a hydrogen
276 atom, the subsequent reactions will lead to formation of $CF_3C(O)H$ in a yield of
277 100 %. As discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can
278 lead to formation of TFA. Thus, the TFA yield from processing of $CHFClCH_2CF_3$
279 is estimated at < 58 %.

280

281 **SI 2.2.7** **HCFC-253fb ($CH_2ClCH_2CF_3$), < 58 % TFA**

282 The atmospheric fate of $CH_2ClCH_2CF_3$ is reaction with OH radicals,
283 followed by reaction with O_2 and RO_2/NO to give $OCHClCH_2CF_3$ or
284 $CH_2ClCH(O)CF_3$ radicals. $OCHClCH_2CF_3$ will decompose to HC(O)Cl and
285 CF_3CH_2 radicals. The latter will undergo further oxidation to give $CF_3C(O)H$.
286 $CH_2ClCH(O)CF_3$ will decompose to give $CF_3C(O)H$ and CH_2Cl radicals.
287 Independent of reaction site for the initial OH-mediated abstraction of a hydrogen
288 atom, the subsequent reactions are expected to give $CF_3C(O)H$ in a yield of 100 %.
289 As discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can lead to
290 formation of TFA. Thus, the TFA yield from processing of $CH_2ClCH_2CF_3$ is
291 estimated at < 58 %.

292

293 **SI 2.2.8** **Halon-2311 (Halothane, $CHBrClCF_3$), 60 ± 10 % TFA**

294	The reaction of OH radicals with $CF_3CHBrCl$ proceeds via abstraction of a
295	hydrogen atom followed by reaction with O_2 and NO, and subsequent Br
296	elimination, to give $CF_3C(O)Cl$ in a yield indistinguishable from 100 %.[23] The
297	estimated tropospheric photolytic lifetime for $CF_3C(O)Cl$ for an overhead sun is 23
298	days.[12] The atmospheric lifetime of $CF_3C(O)Cl$ with respect to uptake and
299	hydrolysis in cloud water is 5-30 days.[9] It has been estimated that, on average, 60
300	% of $CF_3C(O)Cl$ is converted into TFA.[3] The uncertainty on this yield is likely on
301	the order of $\pm$ 10%. Thus, the TFA yield from atmospheric processing of
302	$CF_3CHBrCl$ is estimated at 60 $\pm$10 %.

SI 2.3   HFCs

SI 2.3.1   HFC-125 (CF_3CF_2H), < 10 % TFA

307	The atmospheric fate of CF_3CF_2H is reaction with OH radicals. Reaction
308	with OH produces an alkyl radical that reacts with O_2 to give the peroxy radical
309	$CF_3CF_2O_2$. The peroxy radical reacts with NO/RO_2 to yield the alkoxy radical
310	CF_3CF_2O which decomposes to give COF_2 and CF_3 radicals. However, Ellis *et al.*
311	[19] suggested a mechanism by which $CF_3CF_2O_2$ radicals can react with α-hydrogen
312	containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give CF_3CF_2OH in
313	small amounts (1–10 %).[20] By analogy to the behaviour of other perhaloalcohols,
314	CF_3CF_2OH will eliminate HF to give $CF_3C(O)F$.[21,22] The sole tropospheric fate of
315	$CF_3C(O)F$ is incorporation into water droplets followed by hydrolysis, occurring
316	on a time scale of 5–15 days to give TFA.[9] Thus, the yield of TFA from CF_3CF_2H
317	is estimated as < 10 %.

SI 2.3.2   HFC-134a (CF_3CH_2F), 7–20 % TFA

320	Reaction of OH radicals with CF_3CH_2F yields CF_3CHFO_2 radicals, which
321	react with either other peroxy radicals, RO_2, or NO. Reaction with RO_2 gives
322	CF_3CHFO radicals, which can either decompose or react with O_2 to give $CF_3C(O)F$.
323	The atmospheric fate of $CF_3C(O)F$ is incorporation into water droplets occurring
324	on a time scale of 5–15 days[9] and subsequent hydrolysis yields TFA. Reaction of
325	CF_3CHFO_2 with NO can produce excited alkoxy radicals, CF_3CFHO^*, which
326	undergo rapid decomposition and limit the formation of $CF_3C(O)F$ to a range of 7
327	to 20 %, depending on conditions.[24] Thus, the TFA yield is estimated as 7–20 %.

SI 2.3.3   HFC-143a (CF_3CH_3), < 58 % TFA

330	The atmospheric fate of CH_3CF_3 is reaction with OH radicals. Reaction with
331	OH produces an alkyl radical that reacts with O_2 and NO to yield the alkoxy radical,
332	CF_3CH_2O. The dominant fate of CF_3CH_2O in the atmosphere is reaction with O_2 to
333	give $CF_3C(O)H$ and HO_2.[25] Current understanding of the atmospheric fate of
334	$CF_3C(O)H$ suggests that its atmospheric lifetime is dominated by photolysis. As
335	discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can lead to
336	formation of TFA. Thus, and the TFA yield from processing of CH_3CF_3 is estimated
337	at < 58 %.

SI 2.3.4   HFC-227ea (CF_3CHFCF_3), 100 % TFA

340	The atmospheric fate of CF_3CHFCF_3 is reaction with OH radicals. Reaction
341	with OH produces an alkyl radical that reacts with O_2 and NO to yield the alkoxy
342	radical CF_3CFOCF_3. The atmospheric fate of CF_3CFOCF_3 is decomposition via C-
343	C cleavage to give $CF_3C(O)F$ and CF_3 radicals.[26] The atmospheric fate of

344		CF$_3$C(O)F is incorporation into water droplets followed by hydrolysis to give TFA,
345		occurring on a time scale of 5–15 days.[9] The yield of TFA in the atmospheric
346		degradation of CF$_3$CHFCF$_3$ is 100 %.
347		

344   CF$_3$C(O)F is incorporation into water droplets followed by hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] The yield of TFA in the atmospheric degradation of CF$_3$CHFCF$_3$ is 100 %.

SI 2.3.5   HFC-236cb (CH$_2$FCF$_2$CF$_3$), < 10 % TFA, < 1 % PFPrA

The atmospheric fate of CH$_2$FCF$_2$CF$_3$ is reaction with OH radicals, giving CHFCF$_2$CF$_3$ radicals. These will react with O$_2$ to give CF$_3$CF$_2$CHFO$_2$ radicals, followed by reaction with RO$_2$ or NO to give CF$_3$CF$_2$CHFO. The CF$_3$CF$_2$CHFO radical will either eliminate HC(O)F and produce a shorter perfluorinated alkyl radical CF$_3$CF$_2$, or react with O$_2$ to give CF$_3$CF$_2$C(O)F. The latter only accounts for < 1 % of the fate of CF$_3$CF$_2$CHFO in one atmosphere of air.[27] Thus $\approx$ 100 % of CH$_2$FCF$_2$CF$_3$ is converted into CF$_3$CF$_2$ radicals. These will react with O$_2$ to give the peroxy radical CF$_3$CF$_2$O$_2$. Subsequent reaction with NO/RO$_2$ to yield the alkoxy radical CF$_3$CF$_2$O which decomposes to give COF$_2$ and CF$_3$ radicals. However, Ellis *et al.* [19] suggested a mechanism by which CF$_3$CF$_2$O$_2$ radicals can react with α-hydrogen containing peroxy radicals (e.g., CH$_3$O$_2$) in the atmosphere to give CF$_3$CF$_2$OH in small amounts (1–10 %).[20] By analogy to the behaviour of other perhaloalcohols, CF$_3$CF$_2$OH will eliminate HF to give CF$_3$C(O)F.[21,22] The sole tropospheric fate of CF$_3$C(O)F is incorporation into water droplets followed by hydrolysis, occurring on a time scale of 5–15 days to give TFA.[9] Thus, the yield of TFA from CF$_3$CF$_2$H is estimated as < 10 %.

SI 2.3.6   HFC-236ea (CHF$_2$CHFCF$_3$), $\approx$ 100 % TFA

The atmospheric fate of CHF$_2$CHFCF$_3$ is reaction with OH radicals. There are no studies in the literature of the oxidation mechanism. Reaction will proceed through abstraction of a hydrogen from either the terminal carbon or the central carbon, yielding either CF$_2$CHFCF$_3$ or CHF$_2$CFCF$_3$ radicals, respectively. The former will react with O$_2$ followed by reaction with NO/RO$_2$ to yield the alkoxy radical OCF$_2$CHFCF$_3$, which mainly will decompose to give COF$_2$ and CHFCF$_3$ radicals. CHFCF$_3$ would react further to give CF$_3$C(O)F as the sole product (see discussion for the degradation of HFC-134a, SI section 2.3.2).

The CHF$_2$CFCF$_3$ radical would also react with O$_2$ followed by reaction with NO/RO$_2$, resulting in CHF$_2$COFCF$_3$ radicals, that decompose to CF$_3$C(O)F and CHF$_2$ radicals. The sole tropospheric fate of CF$_3$C(O)F is incorporation into water droplets followed by hydrolysis, occurring on a time scale of 5–15 days to give TFA.[9] The yield of TFA from CHF$_2$CHFCF$_3$ is estimated as $\approx$ 100 %.

SI 2.3.7   HFC-236fa (CF$_3$CH$_2$CF$_3$), (20 ± 10) % TFA

The main atmospheric fate of CF$_3$CH$_2$CF$_3$ is reaction with OH radicals. Reaction of OH radicals with CF$_3$CH$_2$CF$_3$ generate CF$_3$CHCF$_3$ radicals which react with O$_2$ and NO to yield the alkoxy radicals, CF$_3$CHOCF$_3$. The sole fate of CF$_3$CHOCF$_3$ is reaction with O$_2$ to yield CF$_3$C(O)CF$_3$.[28] The likely dominant fate of CF$_3$C(O)CF$_3$ is tropospheric photolysis to give CF$_3$ and CF$_3$C(O) radicals. As discussed in **SI section 2.2.2**, further reaction of CF$_3$C(O) radicals with O$_2$ and HO$_2$ radicals can lead to formation of TFA. Thus, the yield of TFA in the atmospheric oxidation of CF$_3$CH$_2$CF$_3$ is estimated at 20 % (± 10%).

SI 2.3.8   HFC-245fa (CHF$_2$CH$_2$CF$_3$), < 33 % TFA

392	The atmospheric fate of $CHF_2CH_2CF_3$ is reaction with OH radicals.
393	Structure activity relationships (SAR) suggests that approximately 56 % of the
394	reaction of OH radicals with $CHF_2CH_2CF_3$ proceeds through abstraction of a
395	hydrogen from the terminal -CHF_2 group.[12] Subsequent reactions with O_2 and
396	NO/RO_2 lead to the formation of COF_2 and $CF_3C(O)H$ as major products.[29]
397	Abstraction of a hydrogen atom from the -CH_2-group (44 %) is expected to produce
398	a ketone, $CHF_2C(O)CF_3$. By analogy to CF_3COCH_3,[9] the main sink for
399	$CHF_2C(O)CF_3$ is expected to be photolysis, yielding $2 \times COF_2$ and CO_2. However,
400	while it has not been studied, it is possible that $CF_3C(O)$ could be formed as a
401	photolysis fragment. As discussed in **SI section 2.2.2**, further reaction of these
402	CF_3CO radicals with O_2 and HO_2 radicals could lead to additional formation of
403	TFA in small amounts (20 % ($\pm$ 10 %)). Thus, the yield of TFA in the atmospheric
404	oxidation of $CHF_2CH_2CF_3$ is estimated as $0.56 \times < 36 = < 20$ %, plus an additional
405	upper limit range of $0.44 \times (20 \pm 10 \%) = (9 \pm 4)$ %, resulting in an upper limit to
406	the total yield < 33 % TFA.

| 407 | |

SI 2.3.9

408	**SI 2.3.9**	**HFC-329p ($CF_3CF_2CF_2CHF_2$), < 10 % TFA, < 10 % PFPrA, < 10 % PFBA**
409	The atmospheric fate of $CF_3CF_2CF_2CHF_2$ is reaction with OH radicals to
410	give $CF_3CF_2CF_2CF_2$, followed by reaction with O_2 to give $CF_3CF_2CF_2CF_2O_2$
411	radicals. These will undergo reaction with RO_2 or NO to give $CF_3CF_2CF_2CF_2O$
412	with will subsequently eliminate COF_2 and produce a shorter perfluorinated alkyl
413	radical $CF_3CF_2CF_2$. Ellis *et al.*[19] suggested an alternate mechanism where
414	perfluoroalkylperoxy radicals such as $CF_3CF_2CF_2CF_2O_2$ react with α-hydrogen
415	containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give
416	$CF_3CF_2CF_2CF_2OH$ in small amounts (1-10%).[20] By analogy to the behaviour of
417	other perhaloalcohols, $CF_3CF_2CF_2CF_2OH$ will eliminate HF to give
418	$CF_3CF_2CF_2C(O)F$.[21,22] By analogy to $CF_3C(O)F$, the sole fate of $CF_3CF_2CF_2C(O)F$
419	is expected to be incorporation into water droplets followed by hydrolysis,
420	occurring on a time scale of 5–15 days to give PFBA.[9] The shorter $CF_3CF_2CF_2$
421	alkyl radical will undergo the same set of reactions as described above for
422	$CF_3CF_2CF_2CF_2$, including the possibility of $CF_3CF_2CF_2O_2$ reacting with α-
423	hydrogen containing peroxy radicals to give $CF_3CF_2CF_2OH$ in similar small
424	amounts (1–10 %). As discussed above, perhaloalcohols, such as $CF_3CF_2CF_2OH$
425	will eliminate HF to give acyl fluorides, in this case $CF_3CF_2C(O)F$, which will be
426	incorporated into water droplets followed by hydrolysis to give PFPrA. The
427	sequence repeats itself for CF_3CF_2 to give TFA in small amounts (1–10 %). Thus,
428	TFA, PFPrA, and PFBA are all expected to be produced from $CF_3CF_2CF_2CHF_2$ in
429	yields of 1–10 %.

| 430 | |

431	**SI 2.3.10**	**HFC-365mfc ($CF_3CH_2CF_2CH_3$), < 53 % TFA**
432	The atmospheric fate of $CF_3CH_2CF_2CH_3$ is reaction with OH radicals. The
433	only study in the literature on the atmospheric oxidation mechanism of
434	$CF_3CH_2CF_2CH_3$ used Cl atoms as a surrogate for OH radicals. However, based on
435	SAR, approximately 76 % of the reaction of OH radicals, will proceed through
436	abstraction of a hydrogen at the -CH_3 site.[12] Attack on the –CH_3 group, followed
437	by reaction of the resulting alkyl radical with O_2 and the NO/RO_2. This will lead
438	to formation of $CF_3CH_2CF_2C(O)H$.[30] Further oxidation of $CF_3CH_2CF_2C(O)H$ (OH
439	reaction and photolysis) will eventually generate $CF_3C(O)H$ and COF_2 as
440	secondary products.

441 Reaction at the -CH$_2$- group (24 %) would produce a ketone,
442 CF$_3$C(O)CF$_2$CH$_3$. Further oxidation of CF$_3$C(O)CF$_2$CH$_3$ initiated by OH radicals
443 will generate CF$_3$CO radicals (and COF$_2$, CO and CO$_2$). As discussed in **SI section**
444 **2.2.2**, further reaction of CF$_3$CO radicals with O$_2$ and HO$_2$ radicals can lead to
445 formation of TFA in small amounts (20 ± 10%). Thus, the expected yield of TFA
446 in the atmospheric oxidation of CF$_3$CH$_2$CF$_2$CH$_3$ is estimated as 0.76 × (< 58 %) =
447 < 44 %, plus an additional 0.24 × (20 ± 10%) = 5 ± 4%, resulting in an estimated
448 total yield of < 53 % TFA.

449

450 **SI 2.3.11**   **HFC-43-10mee (CF$_3$CF$_2$CFHCFHCF$_3$), 54–60 % TFA, 54–60 % PFPrA**
451 The atmospheric fate of CF$_3$CF$_2$CFHCFHCF$_3$ is reaction with OH radicals.
452 There has been no mechanistic study conducted on the atmospheric degradation of
453 CF$_3$CF$_2$CFHCFHCF$_3$. SAR suggests that approximately half of the reaction
454 proceeds through abstraction of a hydrogen from the -CFH- group, alpha to the
455 terminal CF$_3$ group.[12] Reaction of OH radicals with CF$_3$CF$_2$CFHCFHCF$_3$, followed
456 by reactions with O$_2$ and NO/RO$_2$, is therefore expected to yield both
457 CF$_3$CF$_2$CFOCFHCF$_3$ and CF$_3$CF$_2$CFHCFOCF$_3$ radicals. These will likely undergo
458 decomposition to the give acyl fluorides, CF$_3$CF$_2$C(O)F and CF$_3$C(O)F, and
459 radicals CFHCF$_3$ and CF$_3$CF$_2$CFH. The latter two will react with O$_2$ and RO$_2$/NO
460 yielding CF$_3$CHFO and CF$_3$CF$_2$CHFO radicals. Reaction of CF$_3$CHFO$_2$ and
461 CF$_3$CF$_2$CHFO$_2$ with NO can produce excited alkoxy radicals, which undergo rapid
462 decomposition and limit the overall formation of CF$_3$C(O)F and CF$_3$CF$_2$C(O)F. For
463 CF$_3$CHFO$_2$, the effective yield of CF$_3$CHFO spans a range of 7 to 20 %, depending
464 on conditions.[24] For CF$_3$CF$_2$CHFO, less than 1% is expected to react with O$_2$ and
465 form CF$_3$CF$_2$C(O)F.[27]

466 The decomposition pathways will give CFHO, CF$_3$, and CF$_3$CF$_2$ radicals.
467 Reaction with O$_2$ will lead to CF$_3$C(O)F, and CF$_3$CF$_2$C(O)F. The atmospheric fate
468 of CF$_3$C(O)F, and likely also CF$_3$CF$_2$C(O)F, is incorporation into water droplets
469 followed by hydrolysis to give TFA and PFPrA, occurring on a time scale of 5-15
470 days.[9] Thus, the yield of TFA in the atmospheric oxidation of CF$_3$CF$_2$CFHCFHCF$_3$
471 is estimated as 50 % + ~0.5 × (7–20 %) = 54 – 60 %. A similar yield of PFPrA is
472 also expected.

473

474 **SI 2.4 HFEs/ HCFEs**

475

476 **SI 2.4.1**   **HFE-236ea2 (Desflurane, CF$_3$CHFOCHF$_2$), < 20 % TFA**
477 The atmospheric fate of CF$_3$CHFOCHF$_2$ is reaction with OH radicals. No
478 study of the OH radical initiated oxidation mechanism for CF$_3$CHFOCHF$_2$ exists
479 in the literature. Based on a study of the chlorine atom initiated oxidation, Sulbaek
480 Andersen *et al.*[31] proposed that the hydrogen abstraction reaction proceeds
481 predominantly from the -CHF- carbon group (83 %). This leads to the formation of
482 CHF$_2$OC(O)F and CF$_3$ radicals. Only abstraction of a hydrogen atom from the
483 terminal carbon has the potential to lead to TFA.[31] Abstraction of a hydrogen atom
484 from the terminal carbon (17 %) will generate CF$_3$CHFOCF$_2$ radicals, which will
485 react with O$_2$ and NO to give CF$_3$CHFOCF$_2$O radicals. These will undergo
486 decomposition to give COF$_2$ and CF$_3$CHFO radicals. The latter will in one
487 atmosphere of air react with O$_2$ to give CF$_3$C(O)F (18 %) and HC(O)F (82 %).[31]
488 The atmospheric fate of CF$_3$C(O)F is incorporation into water droplets followed by
489 hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] The TFA yield
490 from atmospheric processing of CF$_3$CHClOCHF$_2$ can be estimated as 0.17 × 0.18

491	$\times$ (100%) = 3 %. To account for possible differences in the location of hydrogen
492	abstraction for the OH mediated abstraction, the upper limit to the TFA yield is
493	estimated at < 20 %.

SI 2.4.2   HFE-347mcf ($C_2F_5CH_2OCHF_2$), < 10 % TFA, < 100 % PFPrA

The atmospheric fate of $C_2F_5CH_2OCHF_2$ is reaction with OH radicals. The reaction proceeds through H abstraction, with the majority of the reaction occurring at the -CH_2- group.[6] This produces a $C_2F_5CHOCHF_2$ radical, which subsequently reacts with O_2 and then with NO/RO_2 to give $C_2F_5C(O)HOCHF_2$ radicals. These will undergo C-C bond scission to give C_2F_5 radicals and $CHF_2OC(O)H$. Alternatively, $C_2F_5C(O)HOCHF_2$ will react with O_2 to give the ester $C_2F_5C(O)OCHF_2$. $C_2F_5C(O)OCHF_2$ may undergo both reaction with OH radicals and uptake into oceans. The lifetime of $C_2F_5C(O)OCHF_2$ regarding OH reaction is likely on the order of a year. Reaction with OH will produce $C_2F_5C(O)OCF_2$ radicals that can undergo COF_2 elimination and produce $C_2F_5C(O)$ or C_2F_5 radicals (+ CO). C_2F_5 radicals cannot be a source of PFPrA. However, Ellis et al. [19] suggested a mechanism by which perfluoroalkylperoxy radicals such as $CF_3CF_2O_2$ react with α-hydrogen containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give CF_3CF_2OH in small amounts (1–10%).[20] By analogy to the behaviour of other perhaloalcohols,[21,22] CF_3CF_2OH will then eliminate HF to give $CF_3C(O)F$ which will undergo hydrolysis to give TFA.[9]

If $C_2F_5C(O)$ is formed from decomposition of the $C_2F_5C(O)OCF_2$ radicals, it will either decompose to give CF_3CF_2 and CO (52 %, in 1 atmosphere of air), or add O_2 to give an acyl peroxy radical, which will react with either NO, NO_2, or HO_2. Reaction with HO_2 gives PFPrA in a yield of 50 %.[7] A yield of ~ 10 % PFPrA from the atmospheric processing of $CF_3CF_2C(O)$ has been estimated by Sulbaek Andersen et al.[32]

Uptake of $C_2F_5C(O)OCHF_2$ into the ocean and hydrolysis will likely occur on a timescale of the order of 1 year[33] and may dominate the removal from the atmosphere. Loss of $C_2F_5C(O)OCHF_2$ via uptake into sea water followed by hydrolysis to give PFPrA is therefore estimated to be a major atmospheric sink for $C_2F_5C(O)OCHF_2$.

Thus, the yield of PFPrA in the atmospheric processing of $C_2F_5CH_2OCHF_2$ is estimated at < 100%, while that of TFA is estimated at < 10 %.

SI 2.4.3   HFE-347mmz1 (Sevoflurane, $(CF_3)_2HCOCH_2F$), < 95 %

The atmospheric fate of $(CF_3)_2HCOCH_2F$ is reaction with OH radicals. No study of the OH radical initiated oxidation mechanism for $CF_3CHFOCH_2F$ exists in the literature. Based on a study of the chlorine atom initiated oxidation, Sulbaek Andersen et al.[31] proposed that the hydrogen abstraction reaction proceeds exclusively from the terminal -CH_2F group. Reaction of the initially formed alkoxy radical with O_2 and NO yields $(CF_3)_2HCOCHFO$, which in one atmosphere of air was found to give 7 % CF_3COCF_3 (through decomposition) and 93 % $(CF_3)_2HCOC(O)F$ (through reaction with O_2). The dominant fate of CF_3COCF_3 is likely tropospheric photolysis to give CF_3 and $CF_3C(O)$ radicals.[12] As discussed in **SI Section 2.2.2**, further reaction of $CF_3C(O)$ radicals with O_2 and HO_2 radicals can lead to formation of TFA in small amounts, and the estimated yield from here can be calculated as 7 % $\times$ (20$\pm$10 %) = 1–2 %.

The major fate of $(CF_3)_2HCOC(O)F$ will be dissolution into surface-water followed by hydrolysis.[34] Hydrolysis would possibly result in the formation of a polyfluorinated ketoacid, $(CF_3)_2HC(O)C(O)OH_{(aq)}$, but it is unclear if the

542	hydrolysis of $(CF_3)_2HCOC(O)F$ would also lead to TFA. Formation of PFPrA is
543	not expected from hydrolysis of $(CF_3)_2HCOC(O)F$. An upper limit for the estimated
544	yield of TFA from ocean uptake and hydrolysis of $(CF_3)_2HCOC(O)F$ is 100%.
545	Thus, the yield of TFA from atmospheric processing of $(CF_3)_2HCOCH_2F$ can be
546	estimated as between 2 % (photolysis of CF_3COCF_3) and an upper limit of 95 %
547	(ocean uptake and hydrolysis of $(CF_3)_2HCOC(O)F$).
548	
549	**SI 2.4.4** **HFE-365mcf3 ($C_2F_5CH_2OCH_3$), < 6% TFA, < 36 % PFPrA**
550	The atmospheric fate of $C_2F_5CH_2OCH_3$ is reaction with OH radicals, which
551	proceeds 44 % at the $-CH_2-$ group and 56 % at the $-CH_3$ group.[35] The alkyl radicals
552	react with O_2, then with NO/RO_2 to give $C_2F_5CH(O)OCH_3$ radicals and
553	$C_2F_5CH_2OCH_2O$ radicals.
554	The main atmospheric fate of $C_2F_5CH(O)OCH_3$ radicals is C-C bond-
555	cleavage to give C_2F_5 radicals and $CH_3OC(O)H$. C_2F_5 radicals add O_2 to give
556	$C_2F_5O_2$ radicals. Ellis _et al._[19] suggested a mechanism by which
557	perfluoroalkylperoxy radicals such as $CF_3CF_2O_2$ react with α-hydrogen containing
558	peroxy radicals (e.g., CH_3O_2) in the atmosphere to give CF_3CF_2OH in small
559	amounts (1–10%).[20] By analogy to the behaviour of other perhaloalcohols,[21,22]
560	CF_3CF_2OH will then eliminate HF to give $CF_3C(O)F$ which will undergo
561	hydrolysis to give TFA.[9]
562	The $C_2F_5CH_2OCH_2O$ radicals will react with O_2 to give the formate
563	$C_2F_5CH_2OC(O)H$. Dissolution into the ocean is a significant tropospheric sink of
564	$CF_3CH_2OC(O)H$,[33] and it is likely it would also be significant for
565	$C_2F_5CH_2OC(O)H$. Hydrolysis would likely give $C_2F_5CH_2OH$, which would be
566	further oxidized to $CF_3CF_2C(O)H$. By analogy to possible aqueous processing of
567	$CF_3C(O)H$, as discussed in **SI section 2.2.2.**, aqueous phase processing of
568	$CF_3CF_2C(O)H$ may lead the formation of PFPrA.
569	Alternatively, OH radicals can react with $C_2F_5CH_2OC(O)H$. This reaction
570	would also lead to the formation of $CF_3CF_2C(O)H$. $CF_3CF_2C(O)H$ has several
571	possible fates in the atmosphere, however photolysis appears to be dominant, with
572	an estimated photolysis lifetime of 0.8 days (this work). Photolysis proceeds via C-
573	C bond scission. The atmospheric lifetime of $CF_3CF_2C(O)H$ with respect to
574	reaction with OH radicals is approximately 23 days.[36] Reaction of $CF_3CF_2C(O)H$
575	with OH gives an acyl radical which will either decompose to give CF_3CF_2 and CO
576	(52 %, in 1 atmosphere of air, or add O_2 to give an acyl peroxy radical,
577	$CF_3CF_2C(O)O_2$, which will react with either NO, NO_2, or HO_2. Reaction with HO_2
578	gives PFPrA in a yield of 50 %.[7] Sulbaek Andersen _et al._[32] evaluated the fates of
579	$CF_3CF_2C(O)$ and estimated a ~ 10 % yield of PFPrA from the atmospheric
580	processing of $CF_3CF_2C(O)$. Including the possibility of $CF_3CF_2C(O)H$ hydrate
581	formation/wet deposition, paralleling the discussion in **SI section 2.2.2**, the yield
582	of PFPrA from processing of $CF_3CF_2C(O)H$ is estimated at < 28 %.
583	In addition to the CF_3CF_2 radicals produced from reactions of $CF_3CF_2C(O)$,
584	the photolysis of $CF_3CF_2C(O)H$ also give CF_3CF_2 radicals. As mentioned above,
585	Ellis _et al._ [19] suggested a mechanism where perfluoroalkylperoxy radicals such as
586	$CF_3CF_2O_2$ react with α-hydrogen containing peroxy radicals (e.g., CH_3O_2) in the
587	atmosphere to give CF_3CF_2OH in small amounts (1–10 %).[20] By analogy to the
588	behaviour of other perhaloalcohols,[21,22] CF_3CF_2OH will eliminate HF to give
589	$CF_3C(O)F$ which will undergo hydrolysis to give TFA.[9]
590	In the absence of any data on the rate of uptake into oceans, we assume here
591	that reaction with OH radicals and loss to the oceans are of equal importance for
592	$C_2F_5CH_2OC(O)H$, the estimated yields of TFA and PFPrA from $C_2F_5CH_2OCH_3$ are

| 593 | (0.44 × (<10) %) + (0.56 × 0.5 × 0.86 × (< 7) %) = < 6 %, and (0.56×50 %) + |
| 594 | (0.56×0.5×28 %)= < 36 %, respectively. |

| 595 | |

SI 2.4.5   HFE-54-11mecf (CF$_3$CHFCF$_2$OCH$_2$C$_2$F$_5$), < 103 % TFA and 25 % PFPrA

The atmospheric fate of CF$_3$CHFCF$_2$OCH$_2$C$_2$F$_5$ is reaction with OH radicals. Whereas the products of this reaction have not been studied, the majority of the reaction is expected to occur at the -CH$_2$- group, leading to the formation of CF$_3$CHFCF$_2$OCH(O$_2$)C$_2$F$_5$ radicals through the subsequent reaction with O$_2$. The peroxy radical with react with NO/RO$_2$ to generate an alkoxy radical that will either decompose to CF$_3$CHFCF$_2$OC(O)H + CF$_2$CF$_3$, or react with O$_2$ to give the ester, CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$

Katsuna et al.[33] showed that dissolution into the oceans followed by hydrolysis is an important fate for C$_2$F$_5$OC(O)H. By analogy, both CF$_3$CHFCF$_2$OC(O)H and CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$ would likely be removed from the atmosphere by reaction with OH as well as loss to the oceans.

Hydrolysis of CF$_3$CHFCF$_2$OC(O)H and CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$ would both result in the formation of CF$_3$CHFCF$_2$OH. The accompanying hydrolysis products would be either HC(O)OH (from CF$_3$CHFCF$_2$OC(O)H) or PFPrA (from CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$)

CF$_3$CHFCF$_2$OH would eliminate HF to give CF$_3$CHFC(O)F and then subsequently, through hydrolysis again, CF$_3$CHFC(O)OH. The fate of CF$_3$CHFC(O)OH in the aqueous environment is unknown, but it is possible that TFA could be a terminal oxidation product.

In summary, hydrolysis of the oxidation products CF$_3$CHFCF$_2$OC(O)H and CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$, would lead to formation of PFPrA and possibly TFA.

Reaction of CF$_3$CHFCF$_2$OC(O)H with OH radicals would lead to the formation of CF$_3$CHF radicals. These will react with O$_2$ to give CF$_3$C(O)F. Reaction of CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$ with OH radicals will lead to the formation of both CF$_3$C(O)F and CF$_2$CF$_3$ radicals. The atmospheric fate of CF$_3$C(O)F is incorporation into water droplets occurring on a time scale of 5–15 days,[9] and subsequent hydrolysis yields TFA. CF$_2$CF$_3$ radicals will react with O$_2$ to give CF$_2$CF$_3$O$_2$. Ellis et al.[19] suggested a mechanism where perfluoroalkylperoxy radicals such as CF$_3$CF$_2$O$_2$ react with α-hydrogen containing peroxy radicals (e.g., CH$_3$O$_2$) in the atmosphere to give CF$_3$CF$_2$OH in small amounts (1–10 %).[20] By analogy to the behaviour of other perhaloalcohols,[21,22] CF$_3$CF$_2$OH will eliminate HF to give CF$_3$C(O)F which will undergo hydrolysis to give TFA.[9]

Thus, formation of both PFPrA and TFA would be expected from the atmospheric degradation of CF$_3$CHFCF$_2$OCH$_2$C$_2$F$_5$. Here is assumed that a) CF$_3$CHFCF$_2$OCH$_2$C$_2$F$_5$ undergoes reaction with OH, producing both CF$_3$CHFCF$_2$OC(O)H and CF$_3$CHFCF$_2$OC(O)CF$_2$CF$_3$ in equal yields, and b) that uptake/hydrolysis and OH reaction are equal fates of both of these oxidation products. These assumptions result in estimated yields of < 103% TFA and 25 % PFPrA. With the current available information, a more quantitative assessment of the yield of TFA and PFPrA is not possible.

SI 2.4.6   HFE-7100 (C$_4$F$_9$OCH$_3$), < 5 % TFA, < 5 % PFPrA, < 55 % PFBA

The atmospheric fate of C$_4$F$_9$OCH$_3$ is reaction with OH radicals leading to the formation of the perfluoroformate C$_4$F$_9$OC(O)H. The lifetime of C$_4$F$_9$OC(O)H with respect to reaction with OH radicals is likely on the order of 2 years.[37] Kutsuna et al.[33] determined that dissolution into the ocean may be an important loss process

643	for the analogous compound, $C_2F_5OC(O)H$, on par with reaction with OH radicals,
644	and it seems likely that loss to the oceans will also be important for $C_4F_9OC(O)H$.
645	Hydrolysis of $C_4F_9OC(O)H$ would yield C_4F_9OH, which would eliminate
646	HF and give $C_3F_7C(O)F$. Hydrolysis of $C_3F_7C(O)F$ would give PFBA.[9]
647	If $C_4F_9OC(O)H$ instead reacts with OH, C_4F_9 radicals will likely be formed.
648	$CF_3CF_2CF_2CF_2$ radicals will add O_2 to give $CF_3CF_2CF_2CF_2O_2$ radicals. These will
649	undergo reaction with RO_2 or NO to give $CF_3CF_2CF_2CF_2O$ with will subsequently
650	eliminate COF_2 and produce a shorter perfluorinated alkyl radical $CF_3CF_2CF_2$. Ellis
651	et al.[19] suggested an alternate mechanism by which the reaction of molecules such
652	as $CF_3CF_2CF_2CF_2O_2$ react with α-hydrogen containing peroxy radicals (e.g.,
653	CH_3O_2) in the atmosphere to give $CF_3CF_2CF_2CF_2OH$ in small amounts (1-10%).[20]
654	By analogy to the behaviour of other perhaloalcohols,[21,22] $CF_3CF_2CF_2CF_2OH$ will
655	eliminate HF to give $CF_3CF_2CF_2C(O)F$. $CF_3CF_2CF_2C(O)F$ will be incorporated
656	into water droplets followed by hydrolysis, occurring on a time scale of 5–15 days
657	to give PFBA.[9] The fraction of $CF_3CF_2CF_2CF_2O_2$ which do not react to produce
658	$CF_3CF_2CF_2CF_2OH$ will end up as $CF_3CF_2CF_2$ radicals (see discussion above).
659	$CF_3CF_2CF_2$ will undergo the same set of reactions as described above, including
660	the possibility of $CF_3CF_2CF_2O_2$ reacting with α-hydrogen containing peroxy
661	radicals to give $CF_3CF_2CF_2OH$ in small amounts (1–10 %). $CF_3CF_2CF_2OH$ will
662	then eliminate HF to give $CF_3CF_2C(O)F$, which will be incorporated into water
663	droplets followed by hydrolysis to give PFPrA. The sequence repeats itself for
664	CF_3CF_2 to give TFA in small amounts (1–10 %). Thus, TFA, PFPrA and PFBA are
665	all expected to be produced from $CF_3CF_2CF_2CF_2O_2$ in yields of < 10 %.
666	Quantitative information on the relative importance of ocean uptake and OH
667	reaction for $C_4F_9OC(O)H$ is not available. Assuming that reaction with OH radicals
668	and loss to the oceans are of equal importance, the following yields from
669	$C_4F_9OC(O)H$ are expected: < 55 % PFBA, < 5 % PFPrA, < 5 % TFA.
670	

671	**SI 2.4.7**	**HFE-7200 ($C_4F_9OC_2H_5$), < 5 % TFA, < 5 % PFPrA, < 55 % PFBA**
672	The atmospheric fate of $C_4F_9OC_2H_5$ is reaction with OH radicals, producing
673	both $C_4F_9OCH(O)CH_3$ and $C_4F_9OCH_2CH_2O$ radicals.[38] The dominant atmospheric
674	fate of $C_4F_9OCH(O)CH_3$ radicals is reaction with O_2 to give the ester
675	$C_4F_9OC(O)CH_3$. $C_4F_9OCH_2CH_2O$ will likely undergo C-C scission to give
676	$HC(O)H$ and $C_4F_9OCH_2$. $C_4F_9OCH_2$ will subsequently react with O_2 and be
677	converted to the formate $C_4F_9OC(O)H$. Attack on the $-CH_2-$ group is judged to be
678	the major reaction site [38] and the ester, $C_4F_9OC(O)CH_3$, is expected to be the major
679	oxidation product.
680	$C_4F_9OC(O)CH_3$ will likely be removed from the atmosphere both by
681	reaction with OH radicals and loss to the oceans. Kutsuna et al.[33] showed that
682	dissolution into the oceans followed by hydrolysis is an important fate for the
683	formate, $C_2F_5OC(O)H$. It seems probable that loss to the oceans is significant for
684	$C_4F_9OC(O)CH_3$. Hydrolysis of $C_4F_9OC(O)CH_3$ will give $CH_3C(O)OH$ and
685	C_4F_9OH. By analogy to the behaviour of other perhaloalcohols,[21,22] The latter will
686	eliminate HF to give $CF_3CF_2CF_2C(O)F$, which will further undergo hydrolysis to
687	give PFBA.[9]
688	Alternatively, reaction of OH radicals with $C_4F_9OC(O)CH_3$ will lead to
689	formation of C_4F_9 radicals. As discussed in **SI section 2.4.7,** atmospheric
690	processing of $CF_3CF_2CF_2CF_2$ radicals will lead to formation of PFBA, PFPrA, and
691	TFA in small amounts (1–10 %). Thus, TFA, PFPrA , and PFBA are expected to
692	be produced from the reaction of OH with $C_4F_9OC(O)CH_3$, all in yields of < 10 %.
693	It remains difficult to access the relative importance of wet
694	deposition/hydrolysis and reaction with OH for $C_4F_9OC(O)CH_3$. Here it is assumed

695		that $C_4F_9OC(O)CH_3$ undergoes reaction with OH at the same rate as wet deposition,
696		resulting in estimated yields < 55 % PFBA, < 5 % PFprA, < 5 % TFA in the
697		atmospheric processing of $C_4F_9OC_2H_5$. With the current available information, a
698		more quantitative assessment of the yield of TFA, PFPrA, and PFBA is not
699		possible.
700		
701	**SI 2.4.8**	**HFE-7300 ($C_2F_5CF(OCH_3)CF(CF_3)_2$), 100 % TFA, 50 % PFPrA**
702		The atmospheric fate of $C_2F_5CF(OCH_3)CF(CF_3)_2$ is reaction with OH
703		radicals leading to the formation of $C_2F_5CF(OCH_2O)CF(CF_3)_2$ radicals. These will
704		undergo reaction with O_2 to form $C_2F_5CF(OC(O)H)CF(CF_3)_2$.[39] The atmospheric
705		lifetime of $C_2F_5CF(OC(O)H)CF(CF_3)_2$ with respect to reaction with OH radicals
706		will likely be in excess of 2 years. Kutsuna et al.[33] have shown that dissolution into
707		the oceans and hydrolysis may be an important fate for $C_2F_5OC(O)H$, and it seems
708		likely that that loss to the oceans is also significant if not dominant for
709		$C_2F_5CF(OC(O)H)CF(CF_3)_2$.
710		Reaction of OH radicals with $C_2F_5CF(OC(O)H)CF(CF_3)_2$ would lead to
711		formation of $C_2F_5CF(O)CF(CF_3)_2$ radicals. These would decompose to give
712		$C_2F_5C(O)F$ and $CF(CF_3)_2$ radicals. The latter would react with O_2, followed by
713		reaction with NO/RO_2 and elimination of CF_3 to give $CF_3C(O)F$. Both $C_2F_5C(O)F$
714		and $CF_3C(O)F$ will undergo incorporation into water droplets followed by
715		hydrolysis to give PFPrA and TFA (100%), respectively, occurring on a time scale
716		of 5–15 days.[9]
717		Hydrolysis of $C_2F_5CF(OC(O)H)CF(CF_3)_2$ would give $HC(O)OH$ and
718		$C_2F_5CF(OH)CF(CF_3)_2$. $C_2F_5CF(OH)CF(CF_3)_2$ would eliminate HF to give the
719		ketone $C_2F_5C(O)CF(CF_3)_2$. The fate of $C_2F_5C(O)CF(CF_3)_2$ (perfluoro(2-methyl)- 3-
720		pentanone) is expected to be photolysis (see **SI section 2.6.2** below) and the yield
721		of TFA from $C_2F_5C(O)CF(CF_3)_2$ is expected to be 101–110 %.
722		It remains difficult to access the relative importance of wet
723		deposition/hydrolysis and reaction with OH for $C_2F_5CF(OC(O)H)CF(CF_3)_2$. If
724		dissolution into the oceans and reaction with OH radicals are assumed to compete
725		equally as fates for $C_2F_5CF(OC(O)H)CF(CF_3)_2$, the estimated yields of TFA and
726		PFPrA from $C_2F_5CF(OCH_3)CF(CF_3)_2$, are 100 % and 50 %, respectively.
727		
728	**SI 2.4.9**	**HFE-7500 ($C_3F_7CF(OC_2H_5)CF(CF_3)_2$), < 110 % TFA, < 10 % PFPrA, < 5 %**
729		**PFBA**
730		The atmospheric fate of $C_3F_7CF(OC_2H_5)CF(CF_3)_2$ is reaction with OH
731		radicals. The majority (> 90 %) of the reaction with OH radicals occurs at the -CH_2-
732		group leading to formation of $C_3F_7CF(OC(O)H)CF(CF_3)_2$.[40] Reaction with O_2 and
733		decomposition via C−C bond scission are competing fates of the
734		$C_3F_7CF(OCH(O)CH_3)CF(CF_3)_2$ radical yielding both a fluorinated acetate, n-
735		$C_3F_7CF(OC(O)CH_3)CF(CF_3)_2$, and a fluorinated formate, n-
736		$C_3F_7CF(OC(O)H)CF(CF_3)_2$. The likely atmospheric fate of these esters will be
737		hydrolysis, producing $C_3F_7CF(OH)CF(CF_3)_2$ and $CH_3C(O)OH/HC(O)OH$.
738		$C_3F_7CF(OH)CF(CF_3)_2$ will undergo heterogeneous decomposition, similar to that
739		of CF_3OH, to give HF and $C_3F_7C(O)CF(CF_3)_2$.[20]
740		The perfluoroketone, $C_3F_7C(O)CF(CF_3)_2$, mentioned above as a hydrolysis
741		product, will undergo photolysis on a timescale of 5–10 days, likely producing
742		C_3F_7 or $C_3F_7C(O)$ radicals, and $CF(CF_3)_2$ or $C(O)CF(CF_3)_2$.
743		As discussed in **SI section 2.4.6** atmospheric processing of C_3F_7 can lead to
744		formation of PFPrA and TFA in small amounts (< 10 %).

The $C_3F_7C(O)$ radicals will either decompose to give $CF_3CF_2CF_2$ and CO (79 % in 1 atmosphere of air)[7] or add O_2 to give an acyl peroxy radical, which will react with either NO, NO_2, or HO_2. Reaction with HO_2 gives PFBA in a yield of 53 %.[7] Assuming that 48 % of $CF_3CF_2CF_2C(O)O_2$ reacts with HO_2 (Sulbaek Andersen, 2024), then the yield of PFBA from atmospheric processing of $C_3F_7C(O)$ can be estimated as approximately 5 %.

$CF(CF_3)_2$ would react with O_2, followed by reaction with NO/RO_2 and elimination of CF_3 to give $CF_3C(O)F$. $CF_3C(O)F$ will undergo incorporation into water droplets followed by hydrolysis to TFA.[9]

The major fate of $C(O)CF(CF_3)_2$ is expected to be elimination of CO to give $CF(CF_3)_2$ (81 % of $CF_3CF_2CF_2C(O)$ radicals undergo CO elimination).[7] Subsequent reactions will produce $CF_3C(O)F$ which will undergo hydrolysis to give 100 % TFA.[9]

Finally, it is germane to consider any potential reaction of OH radicals with $C_3F_7CF(OC(O)CH_3)CF(CF_3)_2$ and $C_3F_7CF(OC(O)H)CF(CF_3)_2$. In both cases, reaction with OH will result in the generation of $CF(CF_3)_2$ radicals and $C_3F_7C(O)F$. These may increase the overall yield of PFPrA in the atmospheric oxidation of $C_3F_7CF(OC_2H_5)CF(CF_3)_2$ and lower the yield of TFA, however, as mentioned above, hydrolysis is expected to be the dominant fate of both esters.

Overall, the estimated yields of TFA, PFPrA, and PFBA are < 110 %, < 10 % and < 5 %, respectively.

SI 2.4.10 **1-ethoxy-1,1,2,2,3,3,3-hepta-fluoro-propane ($C_3F_7OCH_2CH_3$), < 5 % TFA, < 55 % PFPrA**

By analogy to the reactivity of $C_4F_9OC_2H_5$ (see **SI section 2.4.7**),[38] the atmospheric fate of $C_3F_7OCH_2CH_3$ will be reaction with OH radicals. The main site of OH reaction is expected to be the CH_2 group leading to the formation of $C_3F_7OC(O)CH_3$ as the major oxidation product.[38] $C_3F_7OC(O)CH_3$ will likely be removed from the atmosphere both by reaction with OH and loss to the oceans. Kutsuna *et al.*[33] showed that dissolution into the oceans followed by hydrolysis is an important fate for the formate $C_2F_5OC(O)H$. It seems probable that loss to the oceans is significant for $C_3F_7OC(O)CH_3$. Hydrolysis of $C_3F_7OC(O)CH_3$ will give $CH_3C(O)OH$ and C_3F_7OH. The latter will eliminate HF to give $CF_3CF_2C(O)F$,[21,22] which, by analogy to $CF_3C(O)F$, will further undergo hydrolysis to give 100 % PFPrA.[9]

Alternatively, reaction of OH radicals with $C_3F_7OC(O)CH_3$ will lead to formation of C_3F_7 radicals. As discussed in **SI section 2.4.6**, atmospheric processing of C_3F_7 can lead to formation of PFPrA and TFA in small amounts (1-10 %).

It remains difficult to access the relative importance of wet deposition/ hydrolysis and OH reaction as fates of $C_3F_7OC(O)CH_3$. Here is assumed that $C_3F_7OC(O)CH_3$ undergoes reaction with OH at the same rate as wet deposition, resulting in estimated < 55 % PFPrA and < 5 % TFA from the atmospheric processing of $C_3F_7OCH_2CH_3$. With the current available information, a more quantitative assessment of the yield of TFA and PFPrA is not possible.

SI 2.4.11 **HCFE-235da2 (Isoflurane ($CF_3CHClOCHF_2$), $\approx$ 98 % TFA**

The atmospheric oxidation of $CF_3CHClOCHF_2$ proceeds via OH-mediated abstraction of a hydrogen atom. An estimated 95 % of the reaction occurs at the -CHCl- group. Cl elimination subsequently yields the main oxidation product,

795 CF$_3$C(O)OCHF$_2$ (95 ± 3%).[41] The atmospheric lifetime of CF$_3$C(O)OCHF$_2$ with
796 respect to reaction with OH is unknown. The atmospheric lifetime for a similar
797 ester, CF$_3$C(O)OCH$_3$ is approximately 7.5 months.[42, 43] The atmospheric lifetime
798 with respect to reaction with OH is likely to be significantly longer for
799 CF$_3$C(O)OCHF$_2$. Reaction with OH will produce CF$_3$C(O)OCF$_2$ radicals that can
800 undergo COF$_2$ elimination and produce CF$_3$C(O) or CF$_3$ radicals (+ CO). CF$_3$
801 radicals cannot be a source of TFA.

802 Uptake of CF$_3$C(O)OCHF$_2$ into the ocean and hydrolysis will likely occur
803 on a timescale of the order of 1 year[33] and will dominate the removal from the
804 atmosphere. Loss of CF$_3$C(O)OCHF$_2$ via uptake into sea water followed by
805 hydrolysis to give TFA is therefore estimated to be a major atmospheric sink for
806 CF$_3$C(O)OCHF$_2$.[34]

807 The estimated 5 % of the OH reaction that occurs at terminal CHF$_2$ group
808 in CF$_3$CHClOCHF$_2$ will lead to the formation of CF$_3$C(O)Cl. In the troposphere an
809 estimated 60 % of CF$_3$C(O)Cl undergoes hydrolysis yielding TFA.[3]

810 The expected yield of TFA in the atmospheric oxidation of
811 CF$_3$CHClOCHF$_2$ is (95+3) % ≈ 98 %.

812

813 **SI 2.5**   <u>**HFOs/HCFOs/HBFOs**</u>

814

815 Fluorinated olefins have atmospheric lifetimes of typically a few weeks. The
816 deposition of TFA following atmospheric degradation of HFOs/HCFOs/HBFOs is
817 highly spatially heterogeneous as discussed recently by Khan *et al.*[44]

818

819 **SI 2.5.1**   **HFO-1225zc (CF$_2$=CHCF$_3$), < 58 % TFA**
820 Atmospheric oxidation of CF$_2$=CHCF$_3$ proceeds through OH addition to the
821 double bond leading to the formation of OCF$_2$C(OH)HCF$_3$ and HOCF$_2$CH(O)CF$_3$
822 radicals. Decomposition via C-C bond scission is the expected sole fate of
823 OCF$_2$C(OH)HCF$_3$ and HOCF$_2$CH(O)CF$_3$ radicals giving CF$_3$C(O)H in a yield of
824 essentially 100%. As discussed in **SI section 2.22**, atmospheric processing of
825 CF$_3$C(O)H can lead to formation of TFA. Thus, the TFA yield from processing of
826 CF$_3$CF=CH$_2$ is estimated at < 58 %.

827

828 **SI 2.5.2**   **HFO-1234yf (CF$_3$CF=CH$_2$), 100 % TFA**
829 Atmospheric oxidation of CF$_3$CF=CH$_2$ proceeds through OH addition to the
830 double bond. CF$_3$C(O)F is subsequently formed in a yield of 100 %, independent
831 of which side of the double bond is involved in the initial OH-addition step.[45] The
832 tropospheric fate of CF$_3$C(O)F is incorporation into water droplets occurring on a
833 time scale of 5–15 days,[9] and subsequent hydrolysis yields TFA. The yield of TFA
834 in the atmospheric oxidation of CF$_3$CF=CH$_2$ is estimated at 100 %.

835

836 **SI 2.5.3**   **HFO-1234ze(E/Z) (CF$_3$CH=CHF), < 58 % TFA**
837 Atmospheric oxidation of CF$_3$CH=CHF proceeds through OH addition to
838 the double bond.[46] Subsequent reaction with O$_2$ and NO/RO$_2$ leads to the formation
839 of CF$_3$C(O)H and HC(O)F in yields indistinguishable from 100 %. As discussed in
840 **SI section 2.2.2**, atmospheric processing of CF$_3$C(O)H can lead to formation of
841 TFA. Thus, the TFA yield from processing of CF$_3$CH=CHF is estimated at < 58 %.

842

843

844   **SI 2.5.4**   **HFO-1243zf ($CH_2=CHCF_3$), < 58 % TFA**

845   Atmospheric oxidation of $CH_2=CHCF_3$ proceeds through OH addition to
846   the double bond leading to the formation of $CF_3CH(O)CH_2OH$ and
847   $CF_3CHOHCH_2O$ radicals. Decomposition via C-C bond scission is the sole fate of
848   $CF_3CH(O)CH_2OH$ and $CF_3CH(OH)CH_2O$ radicals giving $CF_3C(O)H$ in a yield of
849   essentially 100 %.[47] As discussed in **SI section 2.2.2**, atmospheric processing of
850   $CF_3C(O)H$ can lead to formation of TFA. Thus, the TFA yield from processing of
851   $CF_3CF=CH_2$ is estimated at < 58 %.

852

853   **SI 2.5.5**   **HFO-1336mzz(E/Z) (E-$CF_3CH=CHCF_3$), < 116 % TFA**

854   Atmospheric oxidation of E- and Z- $CF_3CH=CHCF_3$ proceeds through OH
855   addition to the double bond. Østerstrøm et al.[48] used Cl atoms in their study of the
856   atmospheric oxidation of E- and Z- $CF_3CH=CHCF_3$. The OH initiated mechanism
857   has not been studied in detail and remains speculative. The initially formed
858   hydroxy-substituted alkoxy radicals will have competing fates of decomposition
859   and reaction with O_2. It is possible that $CF_3C(O)H$ is formed in this initial step
860   through decomposition, or later through further reactions of possible degradation
861   products, such as $CF_3CH(OH)C(O)CF_3$. An upper limit for the yield of $CF_3C(O)H$
862   is 200 %. As discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$
863   can lead to formation of TFA. Thus, the TFA yield from processing of $CF_3C(O)H$
864   is estimated as 2 × (< 58 %) = < 116 %.

865

866   **SI 2.5.6**   **HFO-1345zfc ($CH_2=CHCF_2CF_3$), < 7 % TFA, < 28 % PFPrA**

867   Atmospheric oxidation of $CH_2=CHCF_2CF_3$ proceeds through OH addition
868   to the double bond leading to the formation of $OCH_2CH(OH)CF_2CF_3$ and
869   $HOCH_2CH(O)CF_2CF_3$ radicals. Decomposition via C-C bond scission is expected
870   to be the sole fate of the $OCH_2CH(OH)CF_2CF_3$ and $HOCH_2CH(O)CF_2CF_3$ radicals
871   giving $CF_3CF_2C(O)H$ in a yield of essentially 100 %.[47] As discussed in **SI section
872   2.4.4** $CF_3CF_2C(O)H$ has several possible fates in the atmosphere with photolysis as
873   the dominant one, resulting in an estimated yield of < 28 % PFPrA and < 7 % TFA
874   from processing of $CF_3CF_2C(O)H$. Thus, the estimated yields of TFA and PFPrA
875   from $CH_2=CHCF_2CF_3$ are < 7 % and < 28 %, respectively.

876

877   **SI 2.5.7**   **HFO-1438mzz(E) ((E)-$CF_3CH=CHCF_2CF_3$), < 65 % TFA, < 28 % PFPrA**

878   Atmospheric oxidation of (E)-$CF_3CH=CHCF_2CF_3$ proceeds through OH
879   addition to the double bond. The initially formed hydroxy-substituted alkoxy
880   radicals will likely have competing fates of decomposition and reaction with O_2. It
881   is possible that both $CF_3C(O)H$ and $CF_3CF_2C(O)H$ are formed in this initial step
882   through decomposition, or later through further reactions of possible degradation
883   products, such as $CF_3CH(OH)C(O)CF_2CF_3$. Upper limits for the yield of
884   $CF_3C(O)H$ and $CF_3CF_2C(O)H$ are 100%. As discussed in **SI section 2.2.2 and
885   2.4.2**, atmospheric processing of $CF_3C(O)H$ and $CF_3CF_2C(O)H$ can lead to
886   formation of TFA and PFPrA: < 58 % and < 28 %, respectively). CF_3CF_2 radicals
887   formed in the degradation of $CF_3CF_2C(O)H$ can lead to formation of CF_3CF_2OH in
888   small amounts (1–10%).[20] CF_3CF_2OH will eliminate HF to give $CF_3C(O)F$ which
889   will undergo hydrolysis to give TFA.[9] To account for both potential pathways of
890   TFA formation, the upper estimated yield of TFA from (E)-$CF_3CH=CHCF_2CF_3$ is
891   < 65 %.

892

893   **SI 2.5.8**   **HFO-1447fz ($CH_2=CHCF_2CF_2CF_3$), < 8 % TFA, < 8 % PFPrA, < 20 % PFBA**

894	Atmospheric oxidation of $CH_2=CHCF_2CF_2CF_3$ proceeds through OH
895	addition to the double bond leading to the formation of $HOCH_2CH(O)CF_2CF_2CF_3$
896	and $OCH_2CH(OH)CF_2CF_2CF_3$ radicals. Decomposition via C-C bond scission is
897	expected to be the sole fate of the $HOCH_2CH(O)CF_2CF_2CF_3$ and
898	$OCH_2CH(OH)CF_2CF_2CF_3$ radicals giving $CF_3CF_2CF_2C(O)H$ in a yield of
899	essentially 100 %.[47]
900	$CF_3CF_2CF_2C(O)H$ has several fates in the atmosphere, including photolysis,
901	reaction with OH and possibly hydrolysis. The lifetime of $CF_3CF_2CF_2C(O)H$ with
902	respect to reaction with OH radicals will be similar to that of $CF_3C(O)H$ (~ 23 days),
903	whereas photolysis is expected to be shorter, 0.5 days (this work). Photolysis
904	proceeds via C-C bond scission to give $CF_3CF_2CF_2$ radicals. Ellis *et al.*[19] suggested
905	that perfluoroalkylperoxy radicals such as $CF_3CF_2CF_2O_2$ can react with α-hydrogen
906	containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give $CF_3CF_2CF_2OH$
907	in small amounts (1–10 %).[20] By analogy to the behaviour of other
908	perhaloalcohols,[21,22] $CF_3CF_2CF_2OH$ will eliminate HF to give $CF_3CF_2C(O)F$ which
909	will undergo hydrolysis to give PFPrA.[9] $CF_3CF_2CF_2O$, which is also generated in
910	the reaction of $CF_3CF_2CF_2O_2$ with RO_2 (or NO), will eliminate COF_2 and give
911	CF_3CF_2 radicals. CF_3CF_2 radicals will add O_2 to give $CF_3CF_2O_2$ radicals which can
912	react with α-hydrogen containing peroxy radicals leading to formation of (1–10 %)
913	CF_3CF_2OH, and thus (1–10 %) TFA.
914	Reaction of $CF_3CF_2CF_2C(O)H$ with OH gives an acyl radical,
915	$CF_3CF_2CF_2C(O)$. As discussed in **SI section 4.2.9**, atmospheric processing of
916	$CF_3CF_2CF_2C(O)$ is estimated to give PFBA in a yield of < 20 %.
917	Including the possibility of hydrate formation, paralleling the discussion in
918	**SI section 2.2.2**. and assuming a lifetime of $CF_3CF_2CF_2C(O)H$ with respect to OH
919	reaction of 23 days, with respect to photolysis of 0.5 days and with respect to
920	deposition and hydrolysis of 2 days, we estimate the yield of PFBA from
921	$CH_2=CHCF_2CF_2CF_3$ to be < 20 %. The yields of TFA and PFPrA are both estimated
922	to be < 8 %.
923	

SI 2.5.9 HCFO-1233zd(E/Z) (E/Z-CF₃CH=CHCl), < 58 % TFA

925	Atmospheric oxidation of E- and Z- $CF_3CH=CHCl$ proceeds through OH
926	addition to the double bond.[49, 50] The atmospheric degradation pathway for
927	$CF_3CH=CHCl$ is complex and produces $CF_3C(O)H$ with estimated yield of 100 %.
928	As discussed in detail in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$
929	can lead to formation of TFA. Thus, the TFA yield from processing of
930	$CF_3CH=CHCl$ is estimated at < 58 %.
931	

SI 2.5.10 2-BTP (CF₃CBr=CH₂), < 58 % TFA

933	Atmospheric oxidation of $CF_3CBr=CH_2$ proceeds through OH addition to
934	the double bond. There is no mechanistic study available in the literature of the
935	atmospheric oxidation of $CF_3CBr=CH_2$. Sulbaek Andersen *et al.*[51] speculate that
936	the OH relation leads to the formation of an enol $CF_3C(OH)=CH_2$ or a
937	carbonyl/alcohol compound, $CF_3C(O)-CH_2OH$. These oxidation products would be
938	reactive towards OH radicals and, in the case of $CF_3C(OH)=CH_2$, possibly undergo
939	keto-enol tautomerization. It is possible that $CF_3C(O)H$ is formed though reaction
940	of OH radicals with the oxidation products or though photolysis of the carbonyl
941	products. An upper limit for the yield of $CF_3C(O)H$ is 100 %. As discussed in **SI**
942	**section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can lead to formation of TFA.
943	Thus, the TFA yield from atmospheric processing of $CF_3CBr=CH_2$ is estimated at
944	< 58 %.

945

SI 2.6   Alcohols/Ketones/Nitriles

947

SI 2.6.1   2,2,2-trifluoroethanol (TFE, CF_3CH_2OH), < 58 % TFA

The atmospheric fate of CF_3CH_2OH is reaction with OH radicals.[37] The resulting CF_3CHOH radical reacts with O_2 to give $CF_3C(O)H$ in a yield of unity.[52] As discussed in **SI section 2.2.2**, atmospheric processing of $CF_3C(O)H$ can lead to formation of TFA. Thus, the TFA yield from processing of $CF_3CF=CH_2$ is estimated at < 58 %.

954

SI 2.6.2   Perfluoro(2-methyl)-3-pentanone ($CF_3CF_2C(O)CF(CF_3)_2$), 101–110 % TFA

The atmospheric oxidation of $CF_3CF_2C(O)CF(CF_3)_2$ has been studied by Taniguchi *et al.*[53] The main atmospheric fate of $CF_3CF_2C(O)CF(CF_3)_2$ is removal by photolysis. Photolysis yields CF_3CF_2 + $C(O)CF(CF_3)_2$ radicals and subsequent reactions of the $C(O)CF(CF_3)_2$ yield $CF_3C(O)F$ in a molar yield of unity. The atmospheric fate of $CF_3C(O)F$ is incorporation into water droplets followed by hydrolysis to give TFA, occurring on a time scale of 5–15 days.[9] CF_3CF_2 will react with O_2 to give $CF_3CF_2O_2$, followed by reaction with NO or RO_2 to give CF_3CF_2O radicals. The latter will eliminate COF_2 to give CF_3 radicals. Ellis *et al.*[19] suggested that perfluoroalkylperoxy radicals such as $CF_3CF_2O_2$ react with α-hydrogen containing peroxy radicals (e.g., CH_3O_2) in the atmosphere to give CF_3CF_2OH in small amounts (1–10 %).[20] By analogy to the behaviour of other perhaloalcohols,[21,22] CF_3CF_2OH will eliminate HF to give $CF_3C(O)F$ which will undergo hydrolysis to give TFA as discussed above.[9] Thus, the yield of TFA in the atmospheric degradation of $CF_3CF_2C(O)CF(CF_3)_2$ is expected to be 101–110 %.

970

SI 6.3   Heptafluorobutyronitrile (($CF_3)_2CFCN$), ≈ 100 % TFA

$(CF_3)_2CFCN$ has a lifetime of 22 years with respect to reaction with OH radicals.[54] Air-sea exchange with the oceanic mixed layer is an important loss mechanism for long lived trace gases if their Henry's law constant is sufficiently large and/or their hydrolysis is base-catalyzed.[55] The extent of ocean uptake and hydrolysis as an environmental sink for $(CF_3)_2CFCN$ is unknown. Reaction with OH radicals gives $CF_3C(O)F$ and COF_2 in a molar yield of 100% during the oxidation of $(CF_3)_2CFCN$.[54] The tropospheric fate of $CF_3C(O)F$ is incorporation into water droplets occurring on a time scale of 5–15 days,[9] and subsequent hydrolysis yields TFA. The yield of TFA in the atmospheric oxidation of $(CF_3)_2CFCN$ is estimated at ≈ 100 %.

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