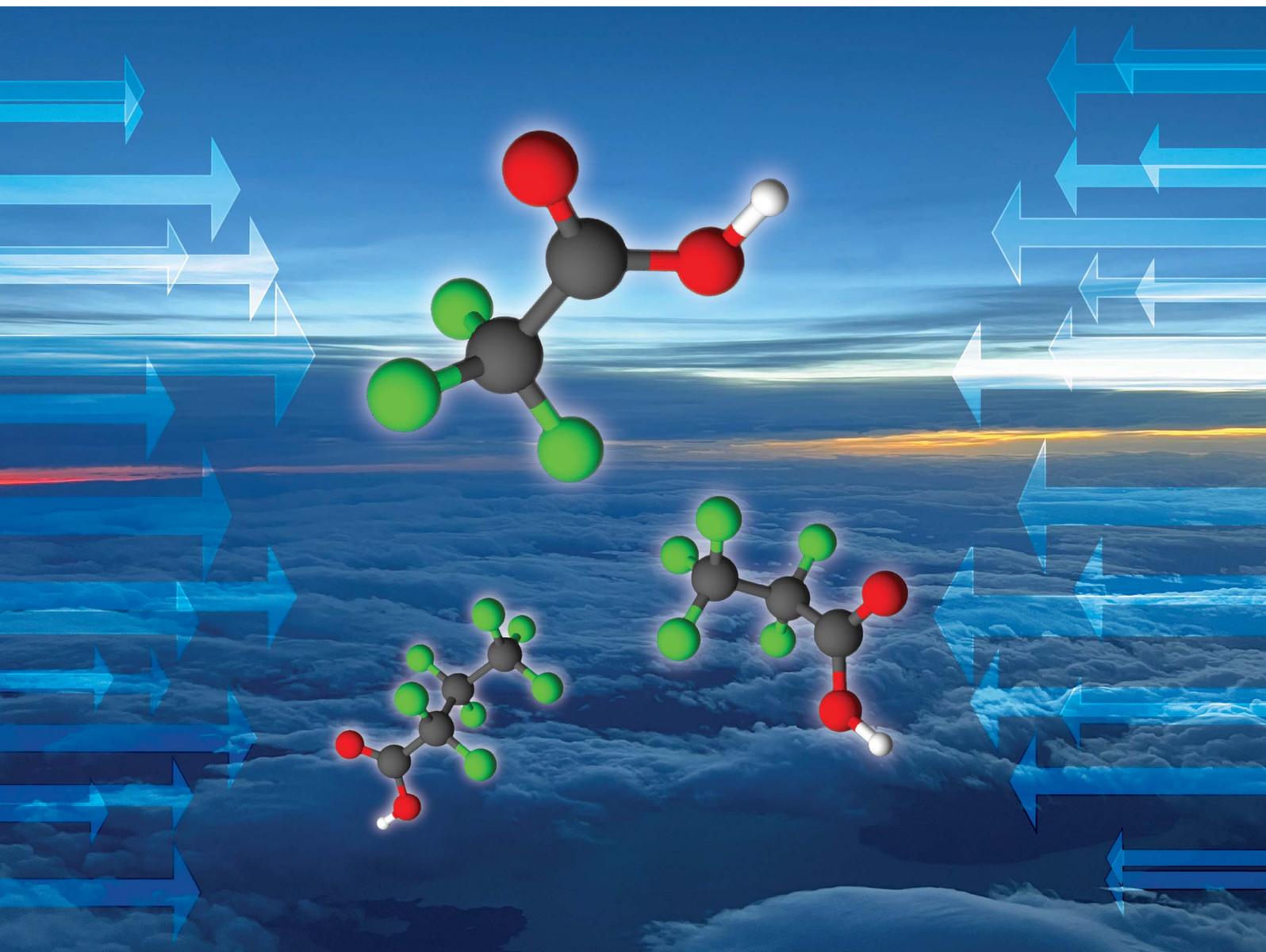


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**PAPER**

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## Yields of perfluorocarboxylic acids from the atmospheric oxidation of Montreal Protocol related gases

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We present here a systematic evaluation of the molar yields of trifluoroacetic acid (TFA), perfluoropropanoic acid (PFPrA), and perfluorobutanoic acid (PFBA) from the atmospheric degradation of gases relevant to the Montreal Protocol and its Amendments. The yields are dependent on the molecular structure of the parent compound and the primary degradation products and radical intermediates formed. We incorporate new data into the Tropospheric Ultraviolet Visible (TUV) model and discuss how recent studies improve our understanding of the relative importance of the photochemical pathways for perfluoroaldehydes,  $C_xF_{2x+1}C(O)H$ , which are key degradation products from some chlorofluorocarbon (CFC) replacement compounds. We identify areas for further research that could advance our understanding of the environmental fate of precursors to short-chain length perfluorocarboxylic acids.

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### Environmental significance

There is substantial scientific, technical, and policy interest in the sources and environmental impacts of trifluoroacetic acid (TFA) and other short chain perfluorocarboxylic acids (PFCAs), which belong to the broader group of chemicals known as per- and polyfluoroalkyl substances (PFAS). Quantifying the anthropogenic contribution to the past, present, and future PFCA loading in the environment requires robust estimates of yields from the atmospheric degradation of volatile fluorinated organic compounds. In this work, we present an updated and expanded evaluation of the molar yields of TFA, perfluoropropanoic acid (PFPrA), and perfluorobutanoic acid (PFBA) in the atmospheric degradation of gases under the purview of the Montreal Protocol and other related gases.

## 1 Introduction

Perfluorocarboxylic acids (PFCAs) are a group of chemicals with the general formula  $C_xF_{2x+1}C(O)OH$ . PFCAs are part of the larger group of chemicals known as per- and polyfluoroalkyl substances (PFAS).<sup>1,2</sup> The ionized form of PFCAs (salts) are ubiquitous contaminants present in precipitation and in river, lake, and ocean water. Concerns have been raised that PFCAs are toxic and threaten global ecosystems and human health. It is well established that long-chain members of the group such as perfluorooctanoic acid ( $C_7F_{15}C(O)OH$ , PFOA) bioaccumulate

and are hazardous. PFOA is regulated as part of national and international agreements.<sup>3,4</sup> However, short-chain members of the group such as trifluoroacetic acid ( $CF_3C(O)OH$ , TFA) do not biomagnify and have been shown to have low toxicity in experimental studies.<sup>5,6</sup> There is current research and regulatory interest in the concentrations of PFAS in the environment, anthropogenic sources, and effects on human and ecosystem health. Robust estimates of yields of PFCAs from the atmospheric degradation of volatile fluorinated organic compounds are essential for quantifying the anthropogenic contribution to the PFCA loading in environment in the past, present, and future.

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), halons, perfluorocarbons (PFCs), hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), hydrobromofluoroolefins (HFBOs), hydrofluoroethers and hydrochlorofluoroethers (HFES/HCFEs) are classes of commercial fluorinated organic compounds. Most of these gases are either controlled, or are substitutes for compounds controlled, by the Montreal Protocol on Substances that Deplete the Ozone Layer and its amendments. These compounds have been released into the atmosphere in significant amounts.<sup>7</sup>

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Some of these compounds can degrade to yield PFCAs.<sup>8</sup> To assess the anthropogenic contribution to the historical, current, and future PFCA loading in the environment, the yields from the atmospheric degradation of volatile fluorinated organic compounds need to be established.<sup>9</sup> Molar yields of TFA from 21 Montreal Protocol-related gases were evaluated by Madronich *et al.*<sup>10</sup> The yields of two other short-chain acids, pentafluoropropionic acid (perfluoropropanoic acid, PFPrA), and heptafluorobutanoic acid (perfluorobutanoic acid, PFBA) were briefly discussed by Madronich *et al.*<sup>11</sup> These are the only PFCAs that can be formed from gases under the purview of the Montreal Protocol and its amendments or from related gases that are in use, but not currently controlled under the Montreal Protocol.<sup>7</sup>

The atmospheric fate of perfluorinated aldehydes is a critical factor in assessments of the yield of PFCAs in the degradation of Montreal Protocol related gases. Since the publication of the previous two assessments,<sup>10,11</sup> new research has been published on the photolysis<sup>12–14</sup> and reaction with OH radicals<sup>15</sup> of  $\text{CF}_3\text{C}(\text{O})\text{H}$ . We incorporate the new data into the Tropospheric Ultraviolet Visible (TUV) model to provide estimates for the importance of photolysis in the atmospheric fate of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  ( $x = 1–3$ ). We discuss how the new studies improve our understanding of the relative importance of the photochemical pathways for perfluorinated aldehydes. We present an updated and expanded assessment of the molar yields of TFA, PFPrA, and PFBA from the atmospheric degradation of Montreal Protocol related gases, including CFCs, HCFCs, HFCs, PFCs, HFOs, HCFOs, HBFOs, HFES, halons, alcohols, and ketones.

## 2 Mechanisms of formation of PFCAs

Fig. 1 shows several possible routes to the formation of PFCAs. The photochemical pathways depend on the molecular structure of the parent compound and the primary degradation products and radical intermediates formed. Compounds with a  $\text{C}_x\text{F}_{2x+1}\text{CF}$ -moiety (where for the purpose of this discussion of gases related to the Montreal Protocol  $x \leq 3$ ) can lead to the formation of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{F}$  as a degradation product.<sup>16</sup> The fate of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{F}$  depends on whether it is formed in the troposphere or the stratosphere. In the troposphere, the sole fate of  $\text{CF}_3\text{C}(\text{O})\text{F}$  is incorporation into water droplets followed by hydrolysis to give TFA (on a time scale of 5–15 days<sup>17</sup>). In the stratosphere, the main fate ( $\approx 90\%$ ) of  $\text{CF}_3\text{C}(\text{O})\text{F}$  is photolysis<sup>18</sup> with the remaining 10% transported to the troposphere where it is removed by hydrolysis.

Compounds with a  $\text{CF}_3\text{CCl}$ -moiety can degrade to give  $\text{CF}_3\text{C}(\text{O})\text{Cl}$ , which undergoes photolysis in competition with incorporation into water droplets. The tropospheric photolytic lifetime for  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  for an overhead sun is estimated to be 23 days.<sup>19</sup> The atmospheric lifetime of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  with respect to uptake and hydrolysis in cloud water is 5–30 days.<sup>17</sup> On average, an estimated 60% of  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  in the troposphere is converted into TFA.<sup>20</sup> If  $\text{CF}_3\text{C}(\text{O})\text{Cl}$  is formed as a degradation product in the stratosphere, its photolytic lifetime is approximately 16 days and conversion to TFA will be of little importance.<sup>8</sup>

Compounds with a perfluoroalkyl group can degrade to give perfluoroalkyl radicals. The sole atmospheric fate of alkyl radicals is addition of  $\text{O}_2$  to give alkylperoxy radicals. Alkylperoxy radicals undergo self- and cross-reactions *via* the Russell mechanism.<sup>21</sup> One channel of the Russell mechanism involves transfer of a hydrogen atom between peroxy radicals which gives alcohol and acyl products. For perfluoroalkylperoxy radicals this channel sets in motion a sequence of reactions leading to PFCAs. In sequence,  $\text{C}_x\text{F}_{2x+1}\text{O}_2$  radicals react with  $\alpha$ -hydrogen containing peroxy radicals (*e.g.*,  $\text{CH}_3\text{O}_2$ ) to give perfluoroalcohols ( $\text{C}_x\text{F}_{2x+1}\text{OH}$ ) that eliminate HF to give perfluoroacylfluorides ( $\text{C}_{x-1}\text{F}_{2x-1}\text{C}(\text{O})\text{F}$ ) which then undergo hydrolysis to give PFCAs.<sup>22</sup> Another channel of the Russell mechanism leads to the formation of alkoxy radicals. Linear perfluoroalkoxy radicals decompose rapidly by eliminating  $\text{COF}_2$  resulting in a perfluoroalkyl radical with one less carbon atom than the parent, *i.e.*, the perfluorinated chain “unzips”. The result in the atmosphere is the formation of a series of PFCAs in small yields (1–10%).<sup>23</sup>

HFES give fluorinated esters as intermediate degradation products. These are removed from the atmosphere by reaction with OH radicals and by dissolution in clouds and seawater. Hydrolysis of fluorinated esters can result in the formation of PFCAs.<sup>24,25</sup>

Finally, compounds with a  $\text{C}_x\text{F}_{2x+1}\text{CH}$ -moiety ( $x \leq 3$ ) can give perfluoroaldehydes,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$ , as a degradation product. These aldehydes are primarily formed from parent compounds whose atmospheric lifetimes are too short to allow transport to the stratosphere to any significant degree. Hence, the degradation of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  generated from Montreal Protocol related gases occurs mainly under tropospheric conditions. Recent studies have improved our understanding of the relative importance of the photochemical pathways leading to formation of PFCAs from  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$ . These are discussed in the following section.

Table 1 summarizes the estimated molar yields of PFCAs (TFA, PFPrA, and PFBA) from the primary degradation products and radical intermediates in the processes described above.

## 3 Fate of $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$ , $x = 1–3$ and the impact on formation of PFCAs

The formation of PFCAs from  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  can occur through several different pathways. Reaction with OH radicals gives  $\text{C}_x\text{F}_{2x+1}\text{CO}$  radicals. This reaction is thought to be a minor sink for  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$ , with an estimated lifetime of approximately 23 days.<sup>15</sup> At 298 K and one atmosphere of air 1%, 50%, and 79% ( $x = 1, 2$ , and 3) of  $\text{C}_x\text{F}_{2x+1}\text{CO}$  radicals decompose to give perfluoroalkyl radicals and CO. The remaining  $\text{C}_x\text{F}_{2x+1}\text{CO}$  radicals add  $\text{O}_2$  to form acylperoxy radicals,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$ .<sup>26</sup> These acylperoxy radicals then react with NO,  $\text{NO}_2$ , and  $\text{HO}_2$ , radicals. Reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  with NO gives perfluorinated acyloxy radicals which decompose by eliminating  $\text{CO}_2$  to give  $\text{C}_x\text{F}_{2x+1}$  radicals. Reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  with  $\text{NO}_2$  gives perfluorinated peroxyacyl nitrates. Reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  radicals leads to the formation of



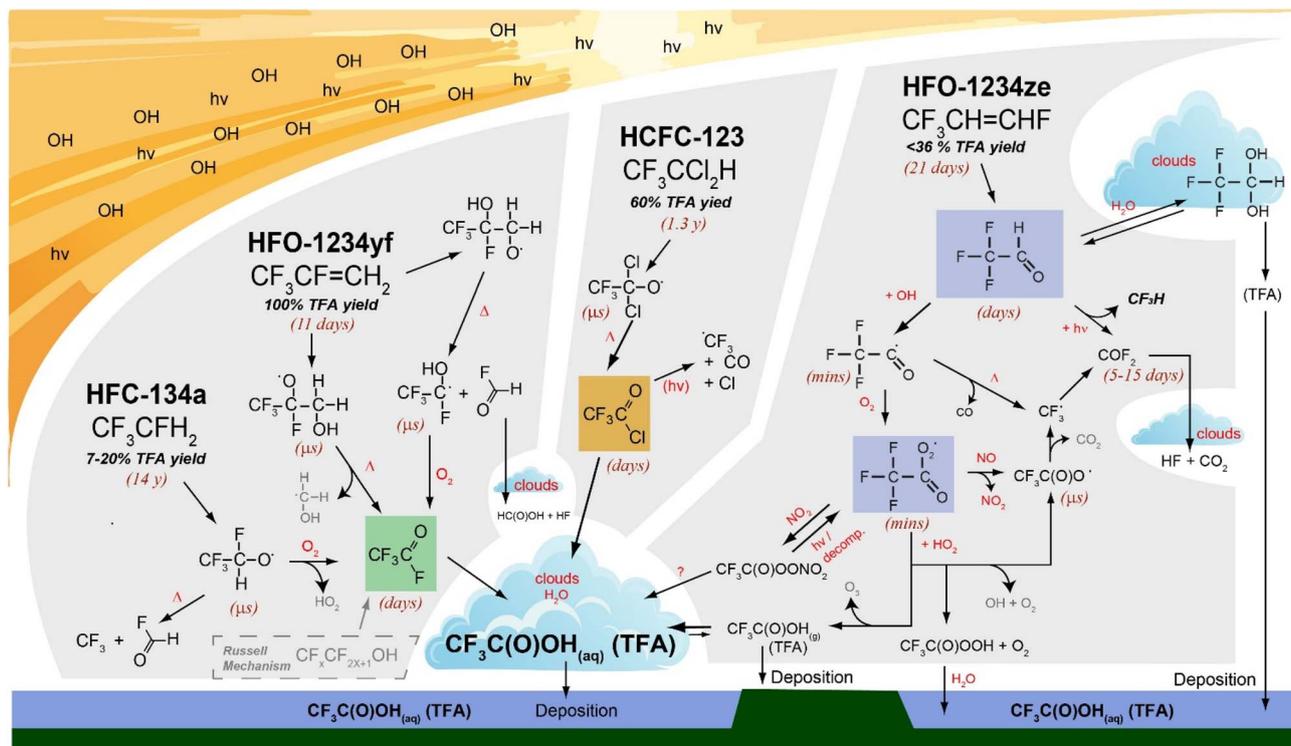


Fig. 1 Key intermediates and degradation pathways leading to formation of TFA during atmospheric degradation of HCFCs, HFCs, HFOs, and HCFOs. Hydrolysis of trifluoroacetylfluoride ( $\text{CF}_3\text{C}(\text{O})\text{F}$ ) and trifluoroacetylchloride ( $\text{CF}_3\text{C}(\text{O})\text{Cl}$ ) leads to TFA in unity molar yield. Hydration of trifluoroacetaldehyde ( $\text{CF}_3\text{C}(\text{O})\text{H}$ ) and reactions of the trifluoroacylperoxyradical ( $\text{CF}_3\text{C}(\text{O})\text{O}_2$ ) can lead to formation of TFA. Approximate atmospheric lifetimes are indicated in parenthesis. In addition (not shown in figure), dissolution and hydrolysis of esters generated in the atmospheric oxidation of HFEs can lead to the formation of TFA. Similar mechanistic pathways lead to the formation of PFPrA and PFBA.

$\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$ , e.g., ( $39 \pm 4\%$  TFA from  $\text{CF}_3\text{C}(\text{O})\text{O}_2$ , at room temperature).<sup>26,32</sup> This reaction is likely temperature dependent. In the analogous reaction of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  radicals with  $\text{HO}_2$ , the channel giving  $\text{CH}_3\text{C}(\text{O})\text{OH}$  increases in importance as the temperature decreases.<sup>33</sup> Hence, the reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  radicals may produce increased yields of PFCA at lower temperatures, but until experimental studies have confirmed this, we chose to use the reported room temperature data.

Perfluorinated peroxyacyl nitrates are relatively stable and can undergo long range transport, e.g., trifluoro peroxyacetyl nitrate ( $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ , FPAN) has a lifetime  $>1$  month above altitudes of about 3 km.<sup>34</sup> Two recent studies have investigated the reaction of FPAN with water vapor to establish the importance of this reaction and the potential molar yield of TFA and/or FPAN hydrate.<sup>35,36</sup>



The formation of TFA was observed in both studies. An upper limit for the rate of the gas-phase reaction of FPAN with  $\text{H}_2\text{O}$  was established and it was concluded that this reaction is unlikely to be an important source of TFA ( $<1\%$ ).<sup>36</sup> Still, the importance of heterogeneous reactions of FPAN with water to

the formation of TFA in the atmosphere are unclear. Similar uncertainty applies to analogous reactions of the larger perfluoro acyl peroxy nitrates  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2\text{NO}_2$ ,  $x = 2$  and 3. Thermal decomposition of FPAN would reform the  $\text{CF}_3\text{C}(\text{O})\text{O}_2$  radical. Thus, FPAN could represent a temporary reservoir for  $\text{CF}_3\text{C}(\text{O})\text{O}_2$  and could impact the distribution of  $\text{CF}_3\text{C}(\text{O})\text{O}_2$  in the atmosphere as a precursor for the formation of TFA (see further discussion below). Until further studies become available, we do not include hydrolysis of acyl peroxy nitrates in our evaluation of the yield of PFCAs from  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$ .

The formation of PFCAs from  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  depends on the local environment and the atmospheric abundance ratio of NO to  $\text{HO}_2$ . The effective yield of TFA from  $\text{CF}_3\text{C}(\text{O})$  in the troposphere was indirectly accessed by Sulbaek Andersen *et al.*<sup>28</sup> in a global modelling study of emissions of HCFO-1233(zd). In their work, the atmospheric lifetimes for  $\text{CF}_3\text{C}(\text{O})\text{H}$  were 2 days and 20 days with respect to photolysis and reaction with OH radicals, respectively. With an overall TFA yield of 2%, the model results of Sulbaek Andersen *et al.* suggest that the molar yield of TFA in the reaction of OH radicals with  $\text{CF}_3\text{C}(\text{O})\text{H}$  (equivalent to considering the yield of TFA from  $\text{CF}_3\text{C}(\text{O})$ ), is on the order of  $\sim 20\%$ . For  $\text{CF}_3\text{CF}_2\text{C}(\text{O})$ , Sulbaek Andersen *et al.*<sup>27</sup> evaluated the importance of the NO/ $\text{HO}_2$  reactions and estimated a  $\sim 10\%$  yield of PFPrA from the reaction of  $\text{HO}_2$  with  $\text{CF}_3\text{CF}_2\text{C}(\text{O})$ . Using the approach of Sulbaek Andersen *et al.*<sup>27</sup> the





**Table 1** Molar yields of PFCAs (TFA, PFPrA, and PFBA) from intermediates and radicals in the degradation of volatile fluorinated organic compounds relevant to the Montreal Protocol. An em dash (—) indicates that no formation (0% molar yield) of the acid is predicted

	Atmospheric fate	Lifetime <sup>e</sup>	Yield estimates (%)			Effective PFCA yield <sup>f</sup> (%)	Notes/references
			TFA	PFPrA	PFBA		
<b>Primary degradation products</b>							
CF <sub>3</sub> C(O)F	UV photolysis (strat. only) Deposition/hydrolysis	≈100 days 5–15 days	— 100	— —	— —	TFA: 10 (strat.)–100 (trop.) TFA: 0 (trop.)–<10 (strat.)	Jubb <i>et al.</i> (2015) <sup>18</sup> Wallington <i>et al.</i> (1994) <sup>17</sup> Jubb <i>et al.</i> (2015) <sup>18</sup>
CF <sub>3</sub> CF <sub>2</sub> C(O)F	UV photolysis (strat. only) <sup>c</sup> Deposition/hydrolysis	≈100 days 5–15 days	1–10 —	100	—	PFPrA: 10 (strat.)–100 (trop.) TFA: 0 (trop.)–<10 (strat.)	Wallington <i>et al.</i> (1994) <sup>17</sup> Jubb <i>et al.</i> (2015) <sup>18</sup>
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> C(O)F	UV photolysis (strat. only) <sup>c</sup> Deposition/hydrolysis	≈100 days 5–15 days	1–10 —	—	100	PFPrA: 0 (trop.)–<10 (strat.) PFBA: 10 (strat.)–100 (trop.)	Wallington <i>et al.</i> (1994) <sup>17</sup>
CF <sub>3</sub> C(O)Cl	UV photolysis <sup>c</sup>	Strat: ~16 days	≤10	—	—	TFA: <10 (strat.)–60 (trop.)	Photolysis branching: CF <sub>3</sub> C(O) + Cl/CF <sub>3</sub> + C(O)Cl Tropospheric fate: Hayman <i>et al.</i> (1994) <sup>20</sup>
CF <sub>3</sub> C(O)H	Deposition/hydrolysis OH reaction <sup>c</sup> UV photolysis Deposition/hydrolysis	Trop: 23 days 5–30 days 23 days 3 days ≥2 days	≤10 100 20 — ≤100	— — — — —	— — — — —	TFA: <58	OH reaction: → CF <sub>3</sub> C(O) ~2% CF <sub>3</sub> C(O) decomp Hurley <i>et al.</i> (2006) <sup>26</sup> Photolysis: >98% CF <sub>3</sub> + HCO OH reaction: → CF <sub>3</sub> CF <sub>2</sub> C(O) ~52% CF <sub>3</sub> CF <sub>2</sub> C(O) decomp Hurley <i>et al.</i> (2006) <sup>26</sup> OH reaction: → CF <sub>3</sub> CF <sub>2</sub> C(O) decomp ~81% CF <sub>3</sub> CF <sub>2</sub> C(O) decomp Hurley <i>et al.</i> (2006) <sup>26</sup>
C <sub>2</sub> F <sub>5</sub> C(O)H	OH reaction <sup>c</sup> UV photolysis <sup>c</sup> Deposition/hydrolysis	23 days 0.8 days ≥2 days	1–10 1–10 —	10 — ≤100	— — —	TFA: <7, PFPrA: <28	OH reaction: → CF <sub>3</sub> C(O) Calvert <i>et al.</i> (2011) <sup>19</sup>
<i>n</i> -C <sub>3</sub> F <sub>7</sub> C(O)H	OH reaction <sup>c</sup> UV photolysis <sup>c</sup> Deposition/hydrolysis	23 days 0.5 days ≥2 days	1–10 1–10 —	1–10 1–10 —	5 — ≤100	TFA: <8 PFPrA: <8, PFBA: <20	OH reaction: → CF <sub>3</sub> CF <sub>2</sub> C(O) Hurley <i>et al.</i> (2006) <sup>26</sup>
CF <sub>3</sub> C(O)CF <sub>3</sub>	Deposition/hydrolysis	≥2 days	—	—	—	TFA: 20 ± 10	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
CHF <sub>2</sub> C(O)CF <sub>3</sub>	UV photolysis <sup>c</sup> Deposition/hydrolysis	27 days n/a	20 ± 10 20 ± 10	— —	— —	TFA: 20 ± 10 TFA: <100	(→ CF <sub>3</sub> C(O) + CF <sub>3</sub> ) Calvert <i>et al.</i> (2011) <sup>19</sup> Kutsuna <i>et al.</i> (2004) <sup>25</sup>
(CF <sub>3</sub> ) <sub>2</sub> HCOC(O)F	Deposition/hydrolysis	n/a	<100	—	—	TFA: <5	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
C <sub>4</sub> F <sub>9</sub> OC(O)H	OH reaction <sup>c</sup> Deposition/hydrolysis	2 years n/a	1–10 —	1–10 —	1–10 100	TFA: <5 PFPrA: <5, PFBA: <55 TFA: 4, PFPrA: 64	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
C <sub>2</sub> F <sub>5</sub> CH <sub>2</sub> OC(O)H	OH reaction <sup>c</sup> Deposition/hydrolysis	n/a n/a	<7 —	<28 100	— —	TFA: 100	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
CF <sub>3</sub> CHF <sub>2</sub> OC(O)H	OH reaction <sup>c</sup> Deposition/hydrolysis	n/a n/a	— 100	— —	— —	TFA: <5, PFPrA: <55 TFA: 4, PFPrA: 64	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
<i>n</i> -C <sub>3</sub> F <sub>7</sub> OC(O)CH <sub>3</sub>	Deposition/hydrolysis OH reaction <sup>c</sup> Deposition/hydrolysis	n/a n/a n/a	100 1–10 —	— 1–10 —	— — —	TFA: <5, PFPrA: <55	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24</sup>
C <sub>4</sub> F <sub>9</sub> OC(O)CH <sub>3</sub>	Deposition/hydrolysis <sup>c</sup> OH reaction <sup>c</sup> Deposition/hydrolysis	n/a n/a n/a	1–10 1–10 —	100 1–10 —	1–10 100	TFA: <5 PFPrA: <5, PFBA: <55 TFA: 100	OH reaction and hydrolysis assumed equally important Kutsuna <i>et al.</i> (2005) <sup>24,25</sup>
CF <sub>3</sub> C(O)OCHF <sub>2</sub>	Deposition/hydrolysis OH reaction <sup>c</sup> Deposition/hydrolysis	>1 year ~1 year ~1 year	<20 100 <10	— — ≈10	— — —	TFA: <10, PFPrA: <100	Hydrolysis assumed dominant Sulbaek Andersen <i>et al.</i> (2024) <sup>27</sup> Kutsuna <i>et al.</i> (2004, 2005) <sup>24,25</sup>
C <sub>2</sub> F <sub>5</sub> C(O)OCHF <sub>2</sub>	OH reaction <sup>c</sup> Deposition/hydrolysis	>1 year ~1 year	<10 —	— 100	— —	TFA: <10, PFPrA: <100	Hydrolysis assumed dominant Sulbaek Andersen <i>et al.</i> (2024) <sup>27</sup> Kutsuna <i>et al.</i> (2004, 2005) <sup>24,25</sup>

Table 1 (Contd.)

	Atmospheric fate	Lifetime <sup>e</sup>	Yield estimates (%)			Effective PFCA yield <sup>b</sup> (%)	Notes/references
			TFA	PFPrA	PFBA		
CF <sub>3</sub> CHFCF <sub>2</sub> OC(O)	OH reaction <sup>c</sup>	n/a	<110	—	—	TFA: 53, PFPrA: 50	Kutsuna <i>et al.</i> (2005), <sup>24</sup> OH reaction and hydrolysis assumed equally important
CF <sub>2</sub> CF <sub>3</sub>	Deposition/hydrolysis	n/a	<100	100	—	—	Kutsuna <i>et al.</i> (2005) <sup>24</sup>
C <sub>3</sub> F <sub>7</sub> CF(OC(O)CH <sub>3</sub> )	OH reaction <sup>c</sup>	n/a	100	—	100	TFA: <110	Hydrolysis assumed dominant
CF(CF <sub>3</sub> ) <sub>2</sub>	Deposition/hydrolysis <sup>c</sup>	n/a	<110	<10	<5	PFPrA: <10, PFBA: <5	Kutsuna <i>et al.</i> (2005), <sup>24</sup> OH reaction and hydrolysis assumed equally important
C <sub>2</sub> F <sub>5</sub> CF(OC(O)H)	OH reaction <sup>c</sup>	>2 years	100	100	—	TFA: 100, PFPrA: 50	Kutsuna <i>et al.</i> (2005), <sup>24</sup> OH reaction and hydrolysis assumed equally important
C <sub>3</sub> F <sub>7</sub> CF(OC(O)H)	OH reaction <sup>c</sup>	n/a	100	—	100	TFA: <110	Kutsuna <i>et al.</i> (2005) <sup>24</sup>
CF(CF <sub>3</sub> ) <sub>2</sub>	Deposition/hydrolysis <sup>c</sup>	n/a	<110	<10	<5	PFPrA: <10, PFBA: <5	Hydrolysis assumed dominant
<b>Radical intermediates</b>							
CF <sub>3</sub> CF <sub>2</sub>	O <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> → TFA	μs	1–10	—	—	TFA: <10	Ellis <i>et al.</i> (2004) <sup>22</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> + CF <sub>2</sub> O + NO <sub>2</sub>	μs	0	—	—	—	—
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub>	O <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> → PFPrA, TFA	μs	1–10	1–10	—	TFA: <10, PFPrA: <10	Ellis <i>et al.</i> (2004) <sup>22</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> CF <sub>2</sub> + CF <sub>2</sub> O + NO <sub>2</sub>	μs	—	—	—	—	—
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	O <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> → PFBA, PFPrA, TFA	μs	1–10	1–10	1–10	TFA: <10	Ellis <i>et al.</i> (2004) <sup>22</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> + CF <sub>2</sub> O + NO <sub>2</sub>	mins	—	—	—	PFPrA: <10, PFBA: <10	—
CF <sub>3</sub> C(O)	O <sub>2</sub> /HO <sub>2</sub> → TFA	mins	39	—	—	TFA: 20 ± 10	~2% CF <sub>3</sub> C(O) undergoes prompt decomp. Hurley <i>et al.</i> (2006) <sup>26</sup> Sulbaek Andersen <i>et al.</i> (2018) <sup>28</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> + CO <sub>2</sub> + NO <sub>2</sub>	mins	—	—	—	—	—
CF <sub>3</sub> CF <sub>2</sub> C(O)	O <sub>2</sub> /HO <sub>2</sub> → PFPrA	mins	—	50	—	PFPrA: ≈ 10	~52% CF <sub>3</sub> CF <sub>2</sub> C(O) undergoes prompt decomp. Hurley <i>et al.</i> (2006) <sup>26</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> CF <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub> <sup>c</sup>	mins	1–10	—	—	—	—
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> C(O)	O <sub>2</sub> /HO <sub>2</sub> → PFBA	mins	—	—	53	PFBA: ≈ 5	~81% CF <sub>3</sub> CF <sub>2</sub> C(O) undergoes prompt decomp. Hurley <i>et al.</i> (2006) <sup>26</sup>
	O <sub>2</sub> /NO → CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub> <sup>c</sup>	sec-mins	1–10	1–10	—	—	—
CF <sub>3</sub> CHFO <sub>2</sub>	+ RO <sub>2</sub> → CF <sub>3</sub> CHFO + RO + O <sub>2</sub> <sup>c</sup>	sec-mins	25–81	—	—	TFA: 7–20	Wallington <i>et al.</i> (1996) <sup>29</sup>
	+ NO → CF <sub>3</sub> CFHO + NO <sub>2</sub> <sup>c</sup>		25–81	—	—	—	Wallington <i>et al.</i> (2017) <sup>30</sup>
	→ CF <sub>3</sub> + HC(O)F + NO <sub>2</sub>		0	—	—	—	- See also reaction below
CF <sub>3</sub> CHFO	+ O <sub>2</sub> → CF <sub>3</sub> C(O)F + HO <sub>2</sub> <sup>c</sup>	μs-ms	25–81	—	—	TFA: 25–81	Pressure/temperature dep
	+ Δ → CF <sub>3</sub> + HC(O)F		0	—	—	—	Wallington <i>et al.</i> (2017) <sup>30</sup>
CF <sub>3</sub> CF <sub>2</sub> HFO	+ O <sub>2</sub> → CF <sub>3</sub> CF <sub>2</sub> C(O)F + HO <sub>2</sub> <sup>c</sup>	μs-ms	—	100	—	TFA: <10, PFPrA: <1	Mogelberg <i>et al.</i> (1997) <sup>31</sup>
	+ Δ → CF <sub>3</sub> CF <sub>2</sub> + HC(O)F <sup>c</sup>		1–10	—	—	—	—

<sup>a</sup> Stratospheric lifetime is a local not a global lifetime. <sup>b</sup> Effective PFCA yields include competitive direct (e.g. wet deposition/hydrolysis) and indirect sources (e.g. further reactions of radical intermediates) in the atmospheric oxidation of the individual species. <sup>c</sup> Loss process forms a product or radical intermediate that leads to the formation of TFA, PFPrA or PFBA.



yield of PFBA from atmospheric processing of  $C_3F_7C(O)$  can be estimated as approximately 5%.

Long *et al.*<sup>37</sup> recently conducted a computational study and suggested that reaction with  $HO_2$  radicals is an important sink for aldehydes in the atmosphere, incl. for  $CF_3C(O)H$ . For  $CF_3C(O)H$ , this reaction would produce a  $\alpha$ -hydroxy substituted peroxy radical, which may undergo further reactions to yield TFA. Presently, there are no experimental data for this reaction, and its atmospheric importance remains unclear. Until experimental data becomes available, we have not included the reaction of  $HO_2$  reaction with  $C_xF_{2x+1}C(O)H$  in our evaluation of the yield of PFCAs from  $C_xF_{2x+1}C(O)H$ .

Photolysis is a major tropospheric sink for  $C_xF_{2x+1}C(O)H$  and dominates in the stratosphere. While there have been few studies of the quantum yields and photolysis lifetimes of  $C_2F_5C(O)H$  and  $n-C_3F_7C(O)H$ , the photolysis of  $CF_3C(O)H$  has been extensively studied recently, largely due to concerns about photochemical production of HFC-23 ( $CHF_3$ ).<sup>38</sup> The photolysis of  $CF_3C(O)H$  in the troposphere proceeds mainly by two channels:

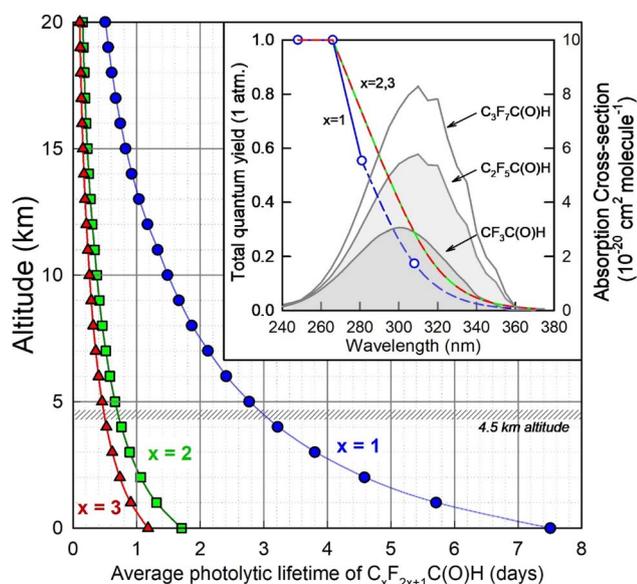
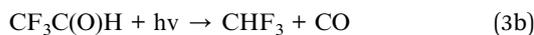
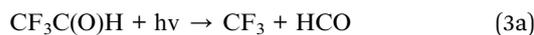


Fig. 2 Estimated average photolytic lifetime using TUV model of  $CF_3C(O)H$  ( $x = 1$ , blue trace/circles),  $C_2F_5C(O)H$  ( $x = 2$ , green trace/squares) and  $n-C_3F_7C(O)H$  ( $x = 3$ , red trace/triangles) from 0 to 20 km at equinox. The hatched horizontal area denotes the density-weighted average altitude of the troposphere of 4.5 km. The insert shows the quantum yields used (at one atmosphere of pressure). For  $CF_3C(O)H$ , linear interpolation is used between the IUPAC recommended pressure dependent quantum yields at 248, 266, and 281 nm (blue solid trace), with an exponential decrease to a long-wavelength limit set to 360 nm. The quantum yields used for  $C_2F_5C(O)H$  and  $C_3F_7C(O)H$  follow those of  $CF_3C(O)H$ , with a shift of 10 nm towards the red (red/green dashed trace). A Stern–Volmer pressure dependency was applied in the TUV for all three compounds. The insert also shows the UV absorbance spectra of  $CF_3C(O)H$ ,  $C_2F_5C(O)H$  and  $C_3F_7C(O)H$ . See text for details.

Photolysis of  $CF_3C(O)H$  is not a source of TFA. Since the evaluation of TFA yields by Madronich *et al.*<sup>10</sup> three papers have been published that provide new measurements of the quantum yields for  $CF_3C(O)H$ .<sup>12–14</sup> The results of these studies have been evaluated by the International Union of Pure and Applied Chemistry (IUPAC) Task Group on Atmospheric Chemical Kinetic Data Evaluation.<sup>39</sup> Estimates in the literature for the atmospheric lifetime for photolysis are in the range  $\sim 2.5$ –13 days.<sup>12,40</sup> Using the updated photochemical parameters, we have reevaluated the photolysis lifetime of  $CF_3C(O)H$ . Atmospheric photolysis coefficients were computed with the Tropospheric Ultraviolet Visible (TUV) model version 5.4, using the pseudo-spherical 4-stream discrete ordinates radiative solver option. Wavelength-dependent data were gridded according to the WMO2 scheme,<sup>41</sup> spanning the range 121–750 nm with enhanced resolution (1 nm) over 220–420 nm to resolve for the strong spectral gradient in tropospheric actinic flux due to stratospheric ozone absorption. The pressure dependence was estimated from the total quantum yields at atmospheric pressure (taken as NTP, normal temperature and pressure), with air number density  $M = 2.45 \times 10^{19}$  molecule  $cm^{-3}$  and the assumption that the reciprocal of the yield decreases linearly to unity at zero pressure (Stern–Volmer) at all wavelengths for which the yield is non-zero. Calculations were made for the Equator and  $40^\circ N$ , 21st March, in 15 min steps and averaged over 24 hours. Atmospheric conditions included cloud-free, aerosol-free skies, 0.1 ground albedo, with an ozone column of 250 Dobson Units at the Equator and 350 Dobson Units for  $40^\circ N$ . For input in the TUV model (see insert in Fig. 2 and SI 1.1), two new data sets were compiled:

(A) A linear interpolation in wavelength between the quantum yield datapoints provided by IUPAC (248, 266, 281 and 308 nm) with a Stern–Volmer pressure dependence.<sup>39</sup> Following the approach of Sulbaek Andersen *et al.* (2023), in this dataset we assume 335 nm for the long-wavelength limit,<sup>12</sup> consistent with the long-wavelength zero point for the quantum yield of  $CH_3C(O)H$ , which has a similar absorption spectrum as  $CF_3C(O)H$ .<sup>42</sup>

(B) A linear interpolation between the quantum yield datapoints provided by IUPAC (248, 266 nm, QY = 1) to 281 nm, with an exponential decrease to a long-wavelength limit set to 360 nm. This approach assigns a more realistic wavelength dependence to the quantum yields at the longer wavelength region, which is particularly important for species that primarily undergo decomposition in the troposphere. The long-wavelength limit reflects the measured  $CF_3C(O)H$  UV spectrum (see insert in Fig. 2).

For models A and B, inclusion of a Stern–Volmer pressure dependence increases the modeled photolysis frequencies resulting in a 20–40% decrease in estimated photolytic lifetime, on average. The actinic flux in the troposphere limits the importance of photolysis at wavelengths below 300 nm. However,  $CF_3C(O)H$  has an absorption maximum at 300 nm, with significant absorption between 300 and 360 nm and modeled atmospheric lifetimes are highly sensitive to the assumed quantum yield fall-off and long-wavelength limit in the region between 308 and 360 nm.



**Table 2** Molar yields of PFCAs (TFA, PFPrA, and PFBA) from volatile fluorinated organic compounds relevant to the Montreal Protocol, see SI for details<sup>a</sup>

Compound	Formula	PFCAs molar yields (%)		
		TFA	PFPrA	PFBA
<b>CFCs<sup>b</sup></b>				
CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	<10	—	—
CFC-114a	CCl <sub>2</sub> FCF <sub>3</sub>	≈ 10	—	—
CFC-216ba	CClF <sub>2</sub> CClFCF <sub>3</sub>	≈ 10	—	—
<b>HCFCs/halons<sup>b</sup></b>				
HCFC-124	CHClFCF <sub>3</sub>	100	—	—
HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	<59	—	—
HCFC-225ca	CF <sub>3</sub> CF <sub>2</sub> CHCl <sub>2</sub>	<10	—	—
HCFC-233fb	CCl <sub>2</sub> FCH <sub>2</sub> CF <sub>3</sub>	<58	—	—
HCFC-243fa	CHCl <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	<58	—	—
HCFC-244fa	CHFClCH <sub>2</sub> CF <sub>3</sub>	<58	—	—
HCFC-253 fb	CH <sub>2</sub> ClCH <sub>2</sub> CF <sub>3</sub>	<58	—	—
Halon-2311 (Halothane) <sup>b</sup>	CHBrClCF <sub>3</sub>	60 ± 10	—	—
<b>HFCs<sup>b</sup></b>				
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	<10	—	—
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	7–20	—	—
HFC-143a	CH <sub>3</sub> CF <sub>3</sub>	<58	—	—
HFC-227ea	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>3</sub>	100	—	—
HFC-236cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> F	<10	<1	—
HFC-236ea	CHF <sub>2</sub> CHF <sub>2</sub> CF <sub>3</sub>	≈ 100	—	—
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	20 ± 10	—	—
HFC-245fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	<33	—	—
HFC-329p	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	<10	<10	<10
HFC-365mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	<53	—	—
HFC-43-10mee	CF <sub>3</sub> CHFCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	54–60	54–60	—
<b>HFEs/HCFEs</b>				
HFE-236ea2 (Desflurane)	CHF <sub>2</sub> OCHF <sub>2</sub> CF <sub>3</sub>	<20	—	—
HFE-347mcf	C <sub>2</sub> F <sub>5</sub> CH <sub>2</sub> OCHF <sub>2</sub>	<10	≈ 10	—
HFE-347mmz1 (Sevoflurane)	(CF <sub>3</sub> ) <sub>2</sub> C(O)HCH <sub>2</sub> F	<95	—	—
HFE-365mcf3	C <sub>2</sub> F <sub>5</sub> CH <sub>2</sub> OCH <sub>3</sub>	<6	<36	—
HFE-54-11mccf	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> C <sub>2</sub> F <sub>5</sub>	<103	25	—
HFE-7100	C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	<5	<5	<55
HFE-7200	C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> H <sub>5</sub>	<5	<5	<55
HFE-7300	C <sub>2</sub> F <sub>5</sub> CF(OCH <sub>3</sub> )CF(CF <sub>3</sub> ) <sub>2</sub>	100	50	—
HFE-7500	C <sub>3</sub> F <sub>7</sub> CF(OC <sub>2</sub> H <sub>5</sub> )CF(CF <sub>3</sub> ) <sub>2</sub>	<110	<10	<5
1-Ethoxy-1,1,2,2,2,3,3,3-hepta-fluoro-propane	C <sub>3</sub> F <sub>7</sub> OCH <sub>2</sub> CH <sub>3</sub>	<5	<55	—
HCFE-235da2 (Isoflurane)	CHF <sub>2</sub> OCHClCF <sub>3</sub>	≈ 98	—	—
<b>HFOs/HCFOs/HBFOs</b>				
HFO-1225zc	CF <sub>2</sub> =CHCF <sub>3</sub>	<58	—	—
HFO-1234yf	CF <sub>3</sub> CF=CH <sub>2</sub>	100	—	—
HFO-1234ze( <i>Z/E</i> )	( <i>E</i> )-CHF=CHCF <sub>3</sub>	<58	—	—
HFO-1243zf	CH <sub>2</sub> =CHCF <sub>3</sub>	<58	—	—
HFO-1336mzz( <i>E/Z</i> )	( <i>E</i> )-CF <sub>3</sub> CH=CHCF <sub>3</sub>	<116	—	—
HFO-1345zfc	CH <sub>2</sub> =CHCF <sub>2</sub> CF <sub>3</sub>	<7	<28	—
HFO-1438mzz( <i>E</i> )	( <i>E</i> )-CF <sub>3</sub> CH=CHCF <sub>2</sub> CF <sub>3</sub>	<65	<28	—
HFO-1447fz	CH <sub>2</sub> =CHCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	<8	<8	<20
HCFO-1233zd( <i>E</i> )	( <i>E</i> )-CF <sub>3</sub> CH=CHCl	<58	—	—
HCFO-1233zd( <i>Z</i> )	( <i>Z</i> )-CF <sub>3</sub> CH=CHCl	<58	—	—
2-Bromo-3,3,3-trifluoro-propene (2-BTP)	CF <sub>3</sub> CBr=CH <sub>2</sub>	<58	—	—
<b>Alcohols/ketones/nitriles</b>				
2,2,2-Trifluoroethanol (TFE)	CF <sub>3</sub> CH <sub>2</sub> OH	<58	—	—
Perfluoro(2-methyl)-3-pentanone	CF <sub>3</sub> CF <sub>2</sub> C(O)CF(CF <sub>3</sub> ) <sub>2</sub>	101–110	—	—
Heptafluorobutyro-nitrile	(CF <sub>3</sub> ) <sub>2</sub> CFCN	≈ 100	—	—

<sup>a</sup> (—) indicates that no formation (0% molar yield) of the acid is predicted. <sup>b</sup> Compounds regulated under the Montreal Protocol and its amendments. Note that Halothane (a Halon) is exempt from regulation under the Montreal Protocol, but a switch by the healthcare industry to non-ozone-depleting alternatives means that emissions are declining.<sup>52</sup>

Fig. 2 includes the trace of the resulting atmospheric photolysis lifetime for CF<sub>3</sub>C(O)H. The troposphere extends to approximately 10 km altitude with a density weighted average

altitude of approximately 4.5 km.<sup>43</sup> At this altitude the average lifetime due to photolysis of CF<sub>3</sub>C(O)H in the lower atmosphere is approximately 3 days. The modeled photolysis frequencies



using either model A or B produce near identical lifetime estimates (see SI Fig. 1.2). This can be explained by the fact that the derivative for the photolysis frequency with respect to wavelength ( $dJ/d\lambda$ ,  $s^{-1} \text{ nm}^{-1}$ ) is significantly larger for model A than model B in the range 308–330 nm, while an approximate equal, but opposite difference is observed for the range 335–360 nm, *i.e.*, the long-wavelength limit region (see SI Fig. 1.3). The region below  $\sim 300$  nm, contributes very little to the photolytic lifetime of  $\text{CF}_3\text{C}(\text{O})\text{H}$ . Notably, the slightly lower 308 nm quantum yield value used in the quantum yield fit by Sulbaek Andersen *et al.*<sup>12</sup> ( $QY = 0.16$  vs.  $0.19$  (IUPAC<sup>39</sup>)) has an amplified impact on the predicted atmospheric lifetime, as this is the regional peak for  $dJ/d\lambda$ .

Relatively few studies have been conducted on the atmospheric lifetime of the longer chain-length perfluoro aldehydes,  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$ .<sup>44,45</sup> For  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$ , Chiappero *et al.*<sup>40</sup> give annual averages for photolysis lifetimes of approximately 0.9 days at 11 km altitude and 2.5 days at 0 km, while Antinolo *et al.*<sup>46</sup> estimate a photolysis lifetime of 3.5 hours at 3.5 km altitude and solar zenith angle of  $16^\circ$  (summertime, noon, Spain). For  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$ , Chiappero *et al.*<sup>40</sup> averaged their measurements for  $\text{CF}_3\text{C}(\text{O})\text{H}$  and  $n\text{-C}_4\text{F}_9\text{C}(\text{O})\text{H}$  and used the resulting wavelength independent photolysis quantum yield (0.11) to estimate annual averages for the atmospheric lifetimes of approximately 0.75 days at 11 km altitude and 2 days at 0 km. Solignac *et al.*<sup>47</sup> studied the photolysis of  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  in the EUPHORE chamber in Valencia, Spain and estimated a photolytic lifetime of close to one day.

It is likely that the photolysis mechanism for  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  will be similar to that of  $\text{CF}_3\text{C}(\text{O})\text{H}$ . The peaks of the UV absorbance for  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  are nearly identical, and both shifted approximately 10 nm to the red in comparison to that of  $\text{CF}_3\text{C}(\text{O})\text{H}$  (see insert in Fig. 2). Here, we use a self-consistent approach to model the photolytic lifetimes  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$ , assuming that the wavelength-dependent quantum yields of  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  are equal to that of  $\text{CF}_3\text{C}(\text{O})\text{H}$ , red-shifted by 10 nm, and following a Stern–Volmer pressure dependency as discussed above. As seen from Fig. 2, the atmospheric lifetimes with respect to photolysis for  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  are shorter than for  $\text{CF}_3\text{C}(\text{O})\text{H}$ , and both less than 1 day (0.8 and 0.5 days at 4.5 km altitude, respectively).

Finally, in addition to photolysis (major sink) and reaction with OH radicals (minor sink),  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  can undergo dry and wet deposition. On contact with liquid water,  $\text{CF}_3\text{C}(\text{O})\text{H}$  reacts to give an aldehyde hydrate (gem-diol,  $\text{CF}_3\text{CH}(\text{OH})_2$ ).<sup>48</sup> The gem-diol, at least in the gas-phase, reacts with OH radicals (lifetime of approximately 90 days) and generates TFA.<sup>48</sup> Unfortunately, key physical parameters needed to estimate dry and wet deposition velocities for  $\text{CF}_3\text{C}(\text{O})\text{H}$  are presently unavailable. Measurements have not been reported for the hydration equilibrium constant, the Henry's Law Constant ( $H$ ), or the effective HLC ( $H^*$ ) for  $\text{CF}_3\text{C}(\text{O})\text{H}$ . Nielsen *et al.*<sup>49</sup> empirically estimated  $H^* > 10^4 \text{ M atm}^{-1}$ , which suggests a wet-deposition lifetime of a few days (4–8 days). Dry deposition may be competitive with wet deposition but is highly dependent on season and geographical location. This, and the absence of

any experimental data for  $\text{CF}_3\text{C}(\text{O})\text{H}$ , renders estimation of dry deposition velocities for  $\text{CF}_3\text{C}(\text{O})\text{H}$  at least as uncertain as those estimated for wet deposition. The atmospheric lifetime of species such as  $\text{HNO}_3$ , which deposit without surface resistance, provides an upper limit for the importance of dry and wet deposition for  $\text{CF}_3\text{C}(\text{O})\text{H}$ .<sup>50</sup> Dry deposition of  $\text{HNO}_3$  occurs on a timescale of 2–3 days, wet deposition in precipitation is more rapid but episodic.<sup>51</sup> We calculate the overall yield of TFA from  $\text{CF}_3\text{C}(\text{O})\text{H}$  by assuming a 2-day lower limit for the deposition lifetime (*i.e.*, upper limit for the importance of dry and wet deposition) and that hydration is efficient, converting  $\text{CF}_3\text{C}(\text{O})\text{H}$  into TFA in a yield of unity (100%). We make the same assumption for the longer chain-length aldehydes,  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$ .

Table 1 includes the estimated molar yields of PFCAs (TFA, PFPrA, and PFBA) from  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  based on the assumptions and caveats for the evaluated atmospheric sinks described above. For  $\text{CF}_3\text{C}(\text{O})\text{H}$ , based on the preceding analysis, we estimate an upper limit of  $<58\%$  molar yield of TFA. The overall yield of TFA would be reduced to 27%, if the upper limit for the estimated wet-deposition lifetime (8 days) was used instead of a 2-day deposition lifetime. The parameterization of wet/dry deposition for  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{H}$  remains a significant source of uncertainty in quantifying an upper limit for PFCa yields.

## 4 Conclusion

A systematic evaluation of the yields of TFA, PFPrA, and PFBA from the atmospheric degradation of gases relevant to the Montreal Protocol and its Amendments is presented. Table 2 lists the estimated overall yields of PFCAs from these compounds. These overall yields are obtained as the sum of the individual contributions from the yields of primary degradation products multiplied by their evaluated yields of PFCAs (see Table 1). Details for the yields of PFCAs for each compound are given in the SI Section 2. A reevaluation of the atmospheric photolytic lifetime for  $\text{CF}_3\text{C}(\text{O})\text{H}$ ,  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$ , and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  leads to revisions in the PFCa yields of many of the species listed in Table 2 from those reported previously.<sup>10,11</sup>

As seen from inspection of the values in Tables 1 and 2, there are substantial uncertainties in many of the estimated yields. For many compounds, it is only possible to provide upper limits for PFCa yields. The uncertainties associated with the yield estimates have two origins. First, inherent uncertainties in the measurements of physical parameters *e.g.* rate coefficients, absorption cross sections, and quantum yields, which are typically 5–20% of the measured values and are relatively straightforward to quantify. Second, for PFCa formation pathways with few, or no, direct measurements available, *e.g.*, wet deposition of  $\text{CF}_3\text{C}(\text{O})\text{H}$ , the yield estimates are based on semi-empirical extrapolations. The uncertainties associated with such extrapolations are significant, difficult to estimate and, in many cases, we can only provide upper limits for PFCa yields.

Without knowledge of the fate of liquid phase  $\text{CF}_3\text{C}(\text{O})\text{H}$ , or its hydrate, after uptake into liquid water and deposition to surface waters, it is difficult to properly evaluate this contribution to the yields of TFA. However, the likely importance of wet



and dry deposition of  $\text{CF}_3\text{C}(\text{O})\text{H}$ , and the possibility that aqueous chemistry of  $\text{CF}_3\text{C}(\text{O})\text{H}$ /hydrates would be an effective source of TFA require that this sink be assessed. Further work to better understand the aqueous chemistry of  $\text{CF}_3\text{C}(\text{O})\text{H}$ /hydrates; hydrolysis of FPAN; quantum yields for photolysis of  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$ , and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  at wavelengths and pressures relevant to the troposphere; and the atmospheric fate of fluorinated esters is also needed. Closing these knowledge gaps will significantly advance our understanding of the environmental fate of precursors to PFCAs such as TFA, PrPFA, and PFBA.

## Author contributions

M. P. Sulbaek Andersen: conceptualization, formal analysis, investigation, methodology visualization, writing – original draft; T. J. Wallington: investigation, writing – review & editing; J. B. Burkholder: investigation, writing – review & editing; S. Madronich: investigation, writing – review & editing; M. L. Hanson: writing – review & editing; D. Van Hooymissen: writing – review & editing; K. R. Solomon: writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data supporting this article have been included as part of the supplementary information (SI). Supplementary information: SI 1  $\text{CF}_3\text{C}(\text{O})\text{H}$ ,  $\text{C}_2\text{F}_5\text{C}(\text{O})\text{H}$  and  $n\text{-C}_3\text{F}_7\text{C}(\text{O})\text{H}$  quantum yields, UV spectra and lifetimes with respect to photolysis. SI 1.1  $\text{CF}_3\text{C}(\text{O})\text{H}$  quantum yields used for TUV models. SI 1.2  $\text{CF}_3\text{C}(\text{O})\text{H}$  lifetimes. SI 1.3 Spectral contributions to the photolysis coefficient of  $\text{CF}_3\text{C}(\text{O})\text{H}$  using the two different quantum yield models (Models A and B). SI 1.4 TUV model data input (tabulated). SI 2 Estimated perfluorocarboxylic acid yields from compounds listed in Table 2. See DOI: <https://doi.org/10.1039/d5ea00179j>.

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