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## Comment on “Assessing the atmospheric fate of trifluoroacetaldehyde (CF<sub>3</sub>CHO) and its potential as a new source of fluoroform (HFC-23) using the AtChem2 box model” by Pérez-Peña *et al.*, *Environ. Sci.: Atmos.*, 2023, 3, 1767–1777, DOI: [10.1039/D3EA00120B](https://doi.org/10.1039/D3EA00120B)

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Recently Pérez-Peña *et al.* published a paper in this journal on the potential atmospheric fate of trifluoroacetaldehyde (CF<sub>3</sub>CHO) as a source of CF<sub>3</sub>H (HFC-23). In their work they utilized both a box model and a global chemistry and transport model to evaluate the production of CF<sub>3</sub>H from the photolysis of CF<sub>3</sub>CHO, the latter generated from photochemical oxidation of HFO-1234ze (CF<sub>3</sub>CH=CHF). Certain chemical assumptions and simplifications were made. We believe the assumptions utilized by Pérez-Peña *et al.* misrepresent the environmental fate of CF<sub>3</sub>CHO. In the following, we present our comments on both the photolysis and the wet and dry deposition of CF<sub>3</sub>CHO. Furthermore, we contemplate the impact of the potential deposition of CF<sub>3</sub>CHO on the formation of trifluoroacetic acid (CF<sub>3</sub>COOH) during the environmental processing of CF<sub>3</sub>CHO.

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### Environmental significance

The question of trifluoromethane (HFC-23) formation in the UV photolysis of trifluoroacetaldehyde has recently become a topic of heightened research interest. Trifluoromethane is a strong greenhouse gas and trifluoroacetaldehyde is a reaction intermediate formed during the degradation of several fluorinated gases, including some commercially important hydrofluoroolefins (HFOs). The atmospheric burden of trifluoromethane is increasing and it is important to know the contribution of HFO chemistry. Pérez-Peña *et al.* (2023) presented an atmospheric model of the degradation of HFO-1234ze (1,3,3,3-tetrafluoropropene), a fourth-generation refrigerant. Their study included several faulty assumptions leading to erroneous conclusions. Here we clarify what those errors are and further discuss the importance of wet and dry deposition as a possible environmental sink for trifluoroacetaldehyde.

## 1. Introduction

Halogenated gases are widely used in many industrial applications. There has been and continues to be a concerted effort to replace traditional CFCs (chlorofluorocarbons) and their replacements with chemicals that minimize the impact on the ozone layer, global climate, and air quality and result in benign atmospheric degradation products. Hydrofluoroolefins (HFOs) are a class of compounds developed in support of this goal. The olefinic double bond provides a site for fast reaction with OH radicals, increasing the OH radical reactivity of HFOs in comparison to those compounds that the HFOs replace. This reduces their atmospheric lifetime, which again leads to small

global warming potentials (GWPs) for the HFOs. CF<sub>3</sub>CHO is a product from the atmospheric degradation of some HFOs.<sup>1</sup> Atmospheric photolysis of CF<sub>3</sub>CHO involves several channels resulting in different molecular fragments and it has been shown that photolysis of CF<sub>3</sub>CHO can produce CF<sub>3</sub>H under certain atmospheric conditions.<sup>2</sup> CF<sub>3</sub>H is a long-lived greenhouse gas (GHG) with a 100 year global warming potential (GWP<sub>100</sub>) of 14 600.<sup>3</sup> Recently, it has also been shown that ozonolysis of some HFOs can produce CF<sub>3</sub>H in molar yields of up to 3%.<sup>4</sup> There is a need for quantification of CF<sub>3</sub>H production from the atmospheric dissemination of HFOs and other halogenated compounds that yield CF<sub>3</sub>CHO as a degradation intermediate. Pérez-Peña *et al.* have recently published a modelling study in this journal on the atmospheric fate of CF<sub>3</sub>CHO as a new source of CF<sub>3</sub>H.<sup>5</sup> This paper is hereinafter referred to as PP23. In that work, the authors employed the AtChem2 v1.2.1 box model with the Master Chemical Mechanism MCMv3.3.1 to model the atmospheric fate of HFO-1234ze (CF<sub>3</sub>CH=CHF) and the GEOS-Chem chemical transport model

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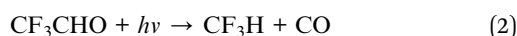
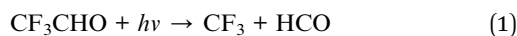
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to estimate deposition rates for CF<sub>3</sub>CHO. Emissions of HFO-1234ze were assumed as 12.6 Gg y<sup>-1</sup> for 2015 and projected to 2050 as 124.4 Gg y<sup>-1</sup>. Two important input parameters for the model are the wavelength and pressure dependent quantum yield of CF<sub>3</sub>H from photolysis of CF<sub>3</sub>CHO, and the Henry's Law Coefficient (HLC) for CF<sub>3</sub>CHO used in the calculations of the wet and dry deposition of CF<sub>3</sub>CHO. We believe errors in the assumptions for these parameters in the model result in an overstatement of the CF<sub>3</sub>H yield in PP23. The following sections discuss the two factors in isolation.

## 2. Overestimating the formation of CF<sub>3</sub>H in CF<sub>3</sub>CHO photolysis

It has been shown that the formation of CF<sub>3</sub>H from CF<sub>3</sub>CHO photolysis (reaction (2)) is only significant in the high atmosphere above 30 km:<sup>2</sup>



The relevant quantum yield,  $\phi_2$ , adopted in the PP23 modelling study are reportedly derived in part from a PhD thesis by Campbell.<sup>6</sup> Part of the thesis has been published in Campbell *et al.*,<sup>7</sup> but the latter publication does not include the study of the molecular channel. Sulbaek Andersen and Nielsen reported an upper limit for the molecular channel yield of 0.3% based on chamber experiments at atmospheric pressure.<sup>8</sup> PP23 used the *upper* limit of <0.3% reported by Sulbaek Andersen and Nielsen<sup>8</sup> as the *lower* limit for  $\phi_2$  in their study, and  $\phi_2 = 0.01$  as a “realistic upper bound” (page 1769 of PP23), extrapolated from data at low-pressure in the non-peer-reviewed thesis. Using the upper limit of Sulbaek Andersen and Nielsen<sup>8</sup> as a lower limit, is puzzling. The 0.003 (0.3%) reported by Sulbaek Andersen and Nielsen<sup>8</sup> is an upper limit for the molar yield of CF<sub>3</sub>H, not the quantum yield ( $\phi_2$  would be on the order of 10<sup>-4</sup> based data shown in Fig. 5 of Sulbaek Andersen and Nielsen<sup>8</sup>). Furthermore, it is unclear how PP23 arrived at their “realistic upper bound” of  $\phi_2 = 0.01$ . There are internal inconsistencies in the reported works of Campbell and coworkers: the thesis states on page 151: “From the fit shown in Fig. 9.2, we extrapolate our measurements to atmospheric pressure, determining a CHF<sub>3</sub> quantum yield of 0.33%, with a lower limit of 0.15% from the 95% confidence bounds on the fit. This measurement is remarkably consistent with the most recent study [*i.e.* Sulbaek Andersen and Nielsen],<sup>8</sup> which determined an upper limit of 0.3% for the atmospheric pressure quantum yield of CHF<sub>3</sub> at 308 nm.” It appears that PP23 may have misinterpreted the conclusions in the Campbell PhD thesis, as well as those of Sulbaek Andersen *et al.*<sup>8</sup> In any event, the choices of PP23 for  $\phi_2$  will substantially overestimate the yield of CF<sub>3</sub>H from the atmospheric photolysis of CF<sub>3</sub>CHO.

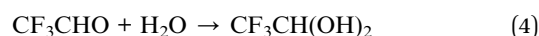
### 2.1 Erroneous Henry's law coefficient for CF<sub>3</sub>CHO

The estimation of CF<sub>3</sub>CHO dry and wet deposition velocities requires knowledge of the air-to-water HLC for CF<sub>3</sub>CHO.

However, as will be discussed below, this term is not simply the ratio ( $H$ ) of aqueous to gas-phase concentrations of the species CF<sub>3</sub>CHO, typically defined as the “intrinsic” HLC:

$$H = [\text{CF}_3\text{CHO}]_{\text{aq}}/[\text{CF}_3\text{CHO}]_{\text{g}} \quad (3)$$

CF<sub>3</sub>CHO forms a stable gem-diol, *i.e.*, hydrate, in the presence of water:



This has been known since the 1930s at least,<sup>9</sup> although the hydrate formation is not discussed explicitly in PP23. The relevant parameter for dry and wet deposition modelling is the “apparent” or “effective” HLC,  $H^*$ , defined by:

$$H^* = \{[\text{CF}_3\text{CHO}]_{\text{aq}} + [\text{CF}_3\text{CH}(\text{OH})_2]_{\text{aq}}\}/[\text{CF}_3\text{CHO}]_{\text{g}} \quad (5)$$

The hydration equilibrium constant is defined as:

$$K_{\text{hyd}} = [\text{CF}_3\text{CH}(\text{OH})_2]_{\text{aq}}/[\text{CF}_3\text{CHO}]_{\text{aq}} \quad (6)$$

Combining and subsequent rearrangement of expressions (3), (5) and (6) gives the effective HLC expressed by  $H$  and  $K_{\text{hyd}}$ :

$$H^* = H(1 + K_{\text{hyd}}) \quad (7)$$

When  $K_{\text{hyd}} \gg 1$ , as will be shown to be the case here, then:

$$H^* \cong H \times K_{\text{hyd}} \quad (8)$$

Neither  $H^*$  nor  $H$  has been measured for CF<sub>3</sub>CHO. The approach used in PP23 to estimate  $H^*$  for CF<sub>3</sub>CHO is flawed for two reasons. First, it relies on “proxy” data derived for CF<sub>3</sub>COF, which is known to hydrolyse rapidly in contact with water to form the highly soluble trifluoroacetic acid, CF<sub>3</sub>COOH (TFA). Second, the values adopted in PP23 are not effective HLCs ( $H^*$ ), but intrinsic ones ( $H$ ). The values were taken from a review paper<sup>1</sup> that cites as its source De Bruyn *et al.*<sup>10</sup> but in fact also includes results from a study by George *et al.*<sup>11</sup> on the uptake of gaseous CF<sub>3</sub>COF to water surfaces. In both studies, the parameter measured was  $H \times k_{\text{rxn}}^{1/2}$ , where  $k_{\text{rxn}}$  is the first-order rate constant for hydrolysis of CF<sub>3</sub>COF. The deconvolution of  $H \times k_{\text{rxn}}^{1/2}$  to yield separate estimates for  $H$  and  $k_{\text{rxn}}$  was subject to very large uncertainties, but the  $H$  values reported in ref. <sup>10</sup> and <sup>11</sup> for CF<sub>3</sub>COF (namely 0.96 and 3.0 M atm<sup>-1</sup>, respectively) were those adopted in PP23 for CF<sub>3</sub>CHO, although the range was extended to 13.17 M atm<sup>-1</sup> by including this value for acetaldehyde, taken to be an “upper bound”. Even if it were reasonable to assume that the intrinsic HLC of the species CF<sub>3</sub>CHO is equal to that of CF<sub>3</sub>COF, the value would need to be multiplied by  $K_{\text{hyd}}$  to give  $H^*$ , the parameter required for deposition velocity estimation.

We suggest here an alternative procedure for estimating  $H^*$  for CF<sub>3</sub>CHO, based on the use of available proxy data for its chlorinated analogue, chloral (CCl<sub>3</sub>CHO). For CCl<sub>3</sub>CHO,  $H^*$  has been reported as a function of temperature.<sup>12</sup> At 25 °C it is  $3.44 \times 10^5$  M atm<sup>-1</sup>.  $H^*(\text{CF}_3\text{CHO})$  can then be estimated from the following equation:



$$H^*(\text{CF}_3\text{CHO})/H^*(\text{CCl}_3\text{CHO}) = \{H(\text{CF}_3\text{CHO})/H(\text{CCl}_3\text{CHO})\} \\ \times \{K_{\text{hyd}}(\text{CF}_3\text{CHO})/K_{\text{hyd}}(\text{CCl}_3\text{CHO})\} \quad (9)$$

The estimation of  $H^*(\text{CF}_3\text{CHO})$  using eqn (9) relies on having sufficient data to derive the ratios:

$$H(\text{CF}_3\text{CHO})/H(\text{CCl}_3\text{CHO}) \quad (10)$$

and

$$K_{\text{hyd}}(\text{CF}_3\text{CHO})/K_{\text{hyd}}(\text{CCl}_3\text{CHO}) \quad (11)$$

For ratio (10) we suggest using as a surrogate the ratio of the HLC of  $\text{CF}_3\text{CH}_2\text{OH}$  to that of  $\text{CCl}_3\text{CH}_2\text{OH}$ , two oxygenated substances that do not form hydrates with water, so their reported HLCs are indeed “intrinsic” ones ( $H$ ). For the purposes of this calculation, the  $H$  values were taken uncritically from the online compilation of HLCs by Sander.<sup>13,14</sup> Although there is considerable uncertainty in the data, warranting a more in-depth assessment of potentially available experimental and QSAR-derived values, here we adopt  $H = 47.6 \text{ M atm}^{-1}$  for  $\text{CF}_3\text{CH}_2\text{OH}$  (originally from JPL recommendations) and  $297 \text{ M atm}^{-1}$  for  $\text{CCl}_3\text{CH}_2\text{OH}$  (average of the 3 values listed). Ratio (10) is therefore taken to be  $47.6/297 = 0.16$ .

For deriving ratio (11) there is also considerable uncertainty. In the case of  $\text{CF}_3\text{CHO}$ , there appears to be only a SPARC-derived  $K_{\text{hyd}}$  value,  $(10^{4.22}) = 1.7 \times 10^4$  from Rayne and Forest.<sup>15,16</sup> Rayne and Forest state that this derived value is close to the one experimental data point available ( $K_{\text{hyd}} = 10^{4.46} = 2.9 \times 10^4$ ) reported by Guthrie.<sup>17</sup> However, their conclusion is erroneous, since the experimental value reported by Guthrie<sup>17</sup> refers to the hydration of  $\text{CCl}_3\text{CHO}$ , not  $\text{CF}_3\text{CHO}$ . Guthrie merely *assumes* it to be valid also for  $\text{CF}_3\text{CHO}$  – in fact, it is taken from a literature review by Le Hénaff,<sup>18</sup> which shows that its true origin is a study by Gruen and McTigue,<sup>19</sup> which actually reports a value of  $2.8 \times 10^4$ .

For  $\text{CCl}_3\text{CHO}$ , apart from the above-mentioned value of  $2.8 \times 10^4$ , there are several other, sometimes greatly conflicting, values for  $K_{\text{hyd}}$ . Herold<sup>20</sup> reported a  $K_{\text{hyd}}$  value of  $>2500$ , according to Gruen and McTigue.<sup>19</sup> Bell and McDougall<sup>21</sup> studied  $\text{CCl}_3\text{CHO}$  hydrate dissociation at concentrations ranging from 0.0014 to 0.123 M in cyclohexane and derived a  $K_{\text{hyd}}$  value of 500. Baymak<sup>22</sup> reported an exceptionally low value for  $K_{\text{hyd}}$  of 25 for  $\text{CCl}_3\text{CHO}$  in aqueous solution, as measured by an electrochemical technique. Finally, in a textbook by Clayden *et al.*<sup>23</sup> a value of  $K_{\text{hyd}} = 2000$  is listed, but the origin of this value is not stated.

Discounting some of these results (organic solvent medium for Bell and McDougall; outlier for Baymak), we will adopt the  $K_{\text{hyd}}$  value from Gruen and McTigue for  $\text{CCl}_3\text{CHO}$  together with that of Rayne and Forest for  $\text{CF}_3\text{CHO}$ . Applying eqn (9):

$$H^*(\text{CF}_3\text{CHO}) = 0.16 \times (1.7 \times 10^4/2.8 \times 10^4) \\ \times 3.44 \times 10^5 \text{ M atm}^{-1} = 3.3 \times 10^4 \text{ M atm}^{-1}$$

This is likely to be an underestimate, since the hydration constant for  $\text{CF}_3\text{CHO}$  used here is lower than that for  $\text{CCl}_3\text{CHO}$ ,

which is contrary to the expectation that the greater electron-withdrawing effect of the fluorine atoms relative to chlorine, combined with their smaller size, and hence lesser steric hindrance towards nucleophilic attack, would suggest a larger  $K_{\text{hyd}}$  for  $\text{CF}_3\text{CHO}$ , than for  $\text{CCl}_3\text{CHO}$ .<sup>23</sup> Nevertheless, the main conclusion is that by adopting a range of HLC values of 0.96 to  $13.17 \text{ M atm}^{-1}$ , the latter based on  $H(\text{CH}_3\text{CHO})$  as an upper bound, PP23 likely underestimates this important parameter by several orders of magnitude.

It should be noted here that  $\text{CF}_3\text{CHO}$  hydrate is a weak acid, dissociating to  $\text{CF}_3\text{CH}(\text{OH})\text{O}^- + \text{H}^+$ .<sup>15,16</sup> However, given its  $\text{p}K_{\text{a}}$  close to 10, dissociation would be negligible under most environmental conditions.<sup>15,16</sup> On the other hand, volatilization of the hydrate (unchanged) from aqueous solution (see below) might impact the *apparent* HLC,  $H^*$ .

## 2.2 The impact of wet and dry deposition of $\text{CF}_3\text{CHO}$

Given the variety and complexity of the parameterizations for wet and dry deposition, it is not immediately obvious what would be the impact of adopting, in AtChem2 with GEOS-Chem or other atmospheric models, the  $H^*$  value for  $\text{CF}_3\text{CHO}$  proposed here, which is greater by more than 4 orders of magnitude than those assumed in PP23, *i.e.* 0.96 and  $3 \text{ M atm}^{-1}$  (together with a value of  $13.17 \text{ M atm}^{-1}$  for acetaldehyde, taken as a upper bound proxy for  $\text{CF}_3\text{CHO}$ ).

Nevertheless, the HLC is known to be a key parameter in estimating both wet and dry deposition and it is reasonable to assume that the far greater HLC would lead to enhanced wet and dry deposition velocities for  $\text{CF}_3\text{CHO}$  and hence, to a correspondingly reduced proportion of photolysis in the atmospheric fate of  $\text{CF}_3\text{CHO}$ , including any possible minor photolysis pathway leading to  $\text{CF}_3\text{H}$  formation.

Some insight into the impact of increasing the HLC from  $13.17 \text{ M atm}^{-1}$  to  $3.3 \times 10^4 \text{ M atm}^{-1}$  can be gained from a generalized study by Bi and Isaacman-VanWertz,<sup>24</sup> which focused mainly on *wet* deposition. As can be seen in Fig. 5 of this paper, the overall timescale for wet deposition (averaged over periods with and without rainfall) declines as the HLC increases, plateauing at a minimum of roughly 100 hours when the HLC exceeds  $10^5 \text{ M atm}^{-1}$ . Assuming that the  $H^*$  value for  $\text{CF}_3\text{CHO}$  is greater than or equal to  $10^4 \text{ M atm}^{-1}$ , as proposed in this work, it is close enough to this low plateau that the overall wet-deposition lifetime may be taken to be  $\sim 100$ –200 hours, or 4–8 days. Using the recommended value of  $k_{\text{OH}} = 5.8 \times 10^{-13} \text{ cm}^3 \text{ per molecule per s}$  at  $25 \text{ }^\circ\text{C}$ ,<sup>25</sup> and  $[\text{OH}] = 1 \times 10^6 \text{ molecule per cm}^3$ ,<sup>26</sup> leads to an average global lifetime for  $\text{CF}_3\text{CHO}$  with respect to OH reaction of 20 days. The relative importance of photolysis compared to OH reaction, as derived from Fig. 4 of PP23, is roughly 3 : 1, implying that the mean photolysis lifetime is about 7 days. Sulbaek Andersen *et al.*<sup>2</sup> estimated the atmospheric lifetime of  $\text{CF}_3\text{CHO}$  with respect to photolysis as  $13 \pm 4$  days. Thus, the wet-deposition lifetime estimated here of 4–8 days, is similar to the mean lifetime due to reaction of  $\text{CF}_3\text{CHO}$  with the OH radical and photolysis. In comparison, the maximum HLC value adopted in PP23, ( $13.17 \text{ M atm}^{-1}$ ) would lead, by extrapolation of the data in Fig. 5 of Bi and Isaacman-



VanWertz,<sup>24</sup> to a wet-deposition lifetime of  $>10^5$  hours ( $>11$  years), making wet deposition completely insignificant.

Dry deposition may also be competitive with wet deposition but is highly dependent on season and ecosystem. Bi and Isaacman-VanWertz<sup>24</sup> also predicted general removal timescales for *dry* deposition, showing a decreasing trend with increasing HLC and reaching a minimum plateau for  $\text{HLC} > 10^5 \text{ M atm}^{-1}$ , in a manner similar to wet deposition. They estimated that, in the particular case of a heavily forested area of the summertime south-eastern U.S., more soluble compounds have dry-deposition lifetimes of only about 7 hours (0.3 days). Furthermore, data presented in Table 1 of Zhang *et al.*<sup>27</sup> show that for compounds with HLCs similar to that proposed here for  $\text{CF}_3\text{CHO}$ , mean dry deposition velocities ( $V_d$ ) are much greater than those assumed in PP23 for  $\text{CF}_3\text{CHO}$  ( $0.024\text{--}0.21 \text{ cm s}^{-1}$ ). For example, the mean  $V_d$  for  $\text{H}_2\text{O}_2$  with an HLC of  $8.7 \times 10^4 \text{ M atm}^{-1}$  (ref. 13) is  $0.643 \text{ cm s}^{-1}$ . This latter value refers to the North America domain, in which deposition is mainly to vegetation-covered land. However, dry deposition to water also needs to be considered, since water covers the greater part of the planet. It is not clear, from Fig. 3 of the ESI of PP23, if dry deposition to the oceans was assessed and included in the model used in PP23.

The potential importance of wet and dry deposition of  $\text{CF}_3\text{CHO}$ , compared to the conclusions of the PP23 study, raises the question of the fate of  $\text{CF}_3\text{CHO}$ , and indeed of its hydrate, in the terrestrial and oceanic environment. It is possible that the hydrates can react with OH in the aqueous phase, thus being a potential source of TFA. It is also possible that the hydrate can undergo biodegradation to trifluoroacetate ions.<sup>28</sup>

### 3. Atmospheric hydration of $\text{CF}_3\text{CHO}$ and fate of the hydrate formed

In the first step of the wet deposition process, atmospheric gaseous  $\text{CF}_3\text{CHO}$  is taken up into cloud droplets and rainwater. Sulbaek Andersen *et al.*<sup>29</sup> performed studies to investigate the subsequent atmospheric fate of the hydrate thus formed, as well as its potential to arise also from the purely gas-phase reaction of  $\text{CF}_3\text{CHO}$  with water vapour. Sulbaek Andersen *et al.* observed that when  $\text{CF}_3\text{CHO}$ -air mixtures were bubbled through water, with a residence time estimated to be roughly 2 seconds (pHs ranging from 2 to 7),  $\text{CF}_3\text{CHO}$  was partially converted into the hydrate form. They also observed gaseous  $\text{CF}_3\text{CHO}$  reacting with water vapour to give the hydrate in smog chamber experiments, although it was suggested that the reaction occurred heterogeneously. An extremely low upper limit to the bimolecular rate constant for the homogeneous reaction was derived. Conversely, when mixtures of gaseous hydrate and air were left in the smog chamber for 22 hours, a 56% decay of the hydrate was observed, giving  $\text{CF}_3\text{CHO}$  in a yield of 100%. In this case too, a heterogeneous reaction was suspected. This thermal gas-phase reversion of the hydrate to the aldehyde was analogous to that reported for  $\text{CCl}_3\text{CHO}$ .<sup>30</sup> Based on the kinetic and product data from the smog chamber study it was concluded that the hydrate would be oxidized quantitatively in the atmosphere to

TFA with a lifetime of approximately 90 days. This is a timescale considerably longer than the wet and dry deposition lifetimes suggested above based on the paper by Bi and Isaacman-VanWertz,<sup>24</sup> and it seems likely that re-incorporation into rain-cloud-seawater will be a significant atmospheric removal mechanism for the hydrate.

Recently Franco *et al.*<sup>31</sup> reported and modelled the analogous atmospheric processing of formaldehyde to formic acid, which was presented as a “previously unknown pathway” by de Gouw and Farmer.<sup>32</sup> The heterogeneous “processing” of  $\text{CF}_3\text{CHO}$  in hydrometeors to its hydrate, followed by desorption of the latter and its subsequent gas-phase oxidation to TFA was not included in the modelling in PP23. Granted, the inclusion of such a mechanism in the model would be hampered by the lack of quantitative characterization of the processes involved. In fact, other regional to global model studies on the atmospheric processing of  $\text{CF}_3\text{CHO}$  from specific HFOs have chosen to omit the wet and dry deposition of  $\text{CF}_3\text{CHO}$  (*e.g.*, Sulbaek Andersen *et al.*<sup>33</sup> Tewari *et al.*<sup>34</sup>).

### 4. Conclusions

We provide here a two-fold reason why the yield of  $\text{CF}_3\text{H}$  reported in PP23, may be greatly overestimated. The lower quantum yield for photolysis of  $\text{CF}_3\text{CHO}$  to give  $\text{CF}_3\text{H}$  and the greatly increased Henry's law coefficient for  $\text{CF}_3\text{CHO}$  proposed here, compared to the values used in PP23, would lead to a lower  $\text{CF}_3\text{H}$  yield on account of the smaller fraction of  $\text{CF}_3\text{CHO}$  undergoing photolysis relative to deposition and OH reaction.

If  $\text{CF}_3\text{CHO}$  is converted into its hydrate, in the atmosphere or after deposition to the Earth's surface, at a rate comparable to those for photolysis and reaction with OH radicals, the hydrate could be a substantial source of TFA. As suggested by Sulbaek Andersen *et al.*,<sup>29</sup> the hydrate could be released from cloud or rain water (*via* Henry's law partitioning or total evaporation of the hydrometeor) followed by atmospheric oxidation to TFA. This latter conclusion tacitly assumes that the gaseous hydrate will not revert to non-hydrated  $\text{CF}_3\text{CHO}$  on a shorter timescale than that required for oxidation. Alternatively, biotic or abiotic transformation of  $\text{CF}_3\text{CHO}$  and its hydrate in the terrestrial or oceanic environment, subsequent to deposition, may also lead to TFA.

Experimental data on  $K_{\text{hyd}}$  and  $H^*$  for  $\text{CF}_3\text{CHO}$  are urgently needed to settle some of these questions. Then further modelling with revised input parameters is warranted.

### Data availability

No new primary research results were generated as part of this review. Alternative analysis and calculations are carried out as explicitly described in the manuscript text using the referenced source material.

### Conflicts of interest

There are no conflicts to declare.



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