COMMENT

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Reply to the 'Comment on "Assessing the atmospheric fate of trifluoroacetaldehyde (CF₃CHO) and its potential as a new source of fluoroform (HFC-23) using the AtChem2 box model"' by O. J. Nielsen, M. P. Sulbaek Andersen and J. Franklin, *Environ. Sci.: Atmos.*, 2025, 5, DOI: 10.1039/D4EA00123K

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In Pérez-Peña *et al.* (DOI: https://doi.org/10.1039/d3ea00120b), we used a suite of box model simulations to determine how trifluoroacetaldehyde (CF₃CHO) produced from HFO-1234ze is lost in the atmosphere and how much fluoroform (CHF₃ or HFC-23) could potentially be produced as a result. For the first time in any modelling study, our simulations included both a minor CF₃CHO photolytic loss channel leading to CHF₃ production and physical removal of CF₃CHO *via* wet and dry deposition. In their comment, Sulbaek Andersen, Nielsen, and Franklin query the assumptions used to simulate these processes. Here, we show that the importance of the photolytic loss pathway remains a matter of community debate and that our results are relatively insensitive to assumptions underlying simulation of deposition. We reiterate the need for measurements of CF₃CHO physical properties to reduce the uncertainties in these processes and pave the way for more sophisticated models.

Environmental significance

Hydrofluoroolefins (HFOs) are increasingly used as refrigerants and blowing agents to replace harmful and banned gases. HFOs are understood to have negligible global warming potential – however, recent experimental studies have identified the potential for some HFOs to contribute to warming through their degradation products. One such HFO is HFO-1234ze (1,1,1,3-tetra fluoropropene), which degrades to trifluoroacetaldehyde (CF₃CHO) and from there may photolyse to produce trifluoromethane (HFC-23), a strong greenhouse gas. In Pérez-Peña *et al.* (2023), we conducted a suite of model sensitivity simulations to estimate HFC-23 production from HFO-1234ze under 14 different scenarios. Our discussion here highlights that the underlying parameters and assumptions remain the subject of community debate and further measurements of CF₃CHO physical properties are urgently needed.

1. Introduction

Hydrofluoroolefins (HFOs) are a family of substances increasingly used as replacement gases for harmful and banned refrigerants and blowing agents because they are understood to have no ozone depleting potential (ODP) and a negligible global warming potential (GWP). Recent experimental studies have called into question the environmental impacts of some HFOs due to the potential of their degradation products to form hydrofluorocarbons (HFCs) with very high GWP.

In Pérez-Peña *et al.*[1] – hereinafter referred to as PP23 – we presented the first attempt to assess the potential implications of this degradation pathway using a box model for a single HFO (HFO-1234ze) and its major degradation product, trifluoroacetaldehyde (CF₃CHO). We used a suite of simulations to test a range of scenarios given the large uncertainties associated with modelling processes with underlying parameters (quantum yields, deposition velocities) that are not well characterised. Our simulations were the first to include any depositional losses of CF₃CHO – prior models have assumed no physical removal of this species *via* either dry or wet deposition processes.[2–4]

The comment by Sulbaek Andersen, Nielsen, and Franklin[5] – hereinafter referred to as SANF25 – queries the assumptions behind two inputs to the box model: the quantum yield of

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fluoroform (CHF_3, also referred to as HFC-23) from photolysis of CF_3CHO and the CF_3CHO deposition velocities. In our suite of sensitivity simulations, we tested a range of values for both inputs, with all assumptions clearly stated in the paper. Below we argue that the tested quantum yield values are entirely appropriate to test model sensitivity, based on the literature available at the time. We accept that the proxy Henry's Law Constants used to derive the CF_3CHO deposition velocities are likely too low but show that substantially higher values make little difference to our results.

2. Quantum yield for CHF_3 production

The yield of CHF_3 from CF_3CHO photolysis ($\phi(CHF_3) = \phi_2$ in PP23) has been somewhat controversial for some years now. PP23 model $\phi(CHF_3) = 0.003$ and 0.01, while SANF25 argue that these values substantially overestimate the yield of CHF_3 from the atmospheric photolysis of CF_3CHO. We accept that SANF25 believe that $\phi(CHF_3) = 0.003$ and $\phi(CHF_3) = 0.01$ are too high, based on their own work. However, the community is not yet accepting. Salierno[6] also reviewed the photochemistry literature on CF_3CHO. Relevant to this discussion, they state: "The methods employed to disprove the formation of HFC-23 from TFE[7] via photolytic decarbonylation are found to be insufficient".

Since our paper was published, there have been two further studies on the quantum yields of CHF_3 production following CF_3CHO photolysis, at tropospherically relevant wavelengths. The unrefereed thesis results of Campbell referred to in both PP23 and SANF25 has now been published,[8] extending the pressure range to 1 bar (N_2 buffer gas), detecting CHF_3 directly, and shows $\phi(CHF_3) = 0.00023 \pm 0.00003$ at 1 bar pressure, rising to $\phi(CHF_3) = 0.0036 \pm 0.0009$ at 0.1 bar and $\phi(CHF_3) = 0.16 \pm 0.03$ under collision-free conditions.

Van Hoomisen et al.[9] also reported $\phi(CHF_3) = 0.00025$ at 308 nm and 1 bar pressure. They also reported significantly higher $\phi(CHF_3) = 0.05$ at 281 nm and 650 Torr pressure, rising to $\phi = 0.114$ at 100 Torr. It is apparent that $\phi(CHF_3)$ is rising significantly for $\lambda < 308$ nm, even within the actinic spectrum in the troposphere.

We maintain that the two quantum yields used in PP23 were not unreasonable as values to test model sensitivity of $\phi(CHF_3)$, at that point in time. We were also very careful in PP23 not to specify $\phi(CHF_3) = 0.003$ as a lower limit, but rather the lower of two reasonable values, based on available literature at the time, to test the dependence of $\phi(CHF_3)$ in our modelling. We remind the reader that PP23 note that the atmospheric yield of CHF_3 is directly proportional to $\phi(CHF_3)$ used in the model, so that other scientists can scale our results by whatever $\phi(CHF_3)$ future studies determine.

3. Wet and dry deposition of CF_3CHO

Our study in PP23 was the first to consider depositional losses of CF_3CHO. Previous efforts to model the atmospheric fate of CF_3CHO have neglected wet and dry deposition entirely,[2–4] as

acknowledged in SANF25. As we articulate in the original article, this is because there are no existing measurements or estimates of the parameters required to calculate CF_3CHO deposition fluxes, making any estimates of the fluxes both challenging and uncertain.

In PP23, we used AtChem2, which is a box model, to simulate the fates of CF_3CHO. AtChem2 uses a single deposition velocity (V_{dep}) to account for gas molecules removed via depositional process (both wet and dry). The connection between Henry's Law constants (H^{cp} in PP23 $= H^*$ in SANF25) and wet and dry deposition, captured in AtChem2 as a single V_{dep} value, is complex, non-linear, and dependent on global atmospheric and surface layer conditions. It is not possible to calculate a global V_{dep} directly from H^{cp}, and neither V_{dep} nor H^{cp} for CF_3CHO have been measured.

In PP23, we used GEOS-Chem modelling to extract representative values for V_{dep} that accounted for both wet and dry deposition for use in AtChem2. As models do not typically represent wet deposition fluxes using a V_{dep} construct, we incorporated a wet deposition contribution based on the globally averaged relationship between wet and dry deposition for proxy species. We then produced three deposition scenarios based on values of $V_{dep} = 0.024$, 0.08 and 0.21 cm s^{-1}. We agree with the SANF25 comment that the proxy H^{cp} used in our paper is likely too low. The question is whether our values of V_{dep}, and hence our subsequent results, misrepresent the fate of CF_3CHO.

To understand the implications of a higher H^{cp} for the fate of CF_3CHO, we explore the potential impacts of using $H^{cp} \approx 3.3 \times 10^4$ M atm^{-1}, as estimated by SANF25 using a different proxy species. The question to be addressed is what the impact is on V_{dep}, and hence on deposition fraction. SANF25 addressed this in their comment using values from Fig. 5 in Bi and Isaacman-VanWertz.[10] It should be noted that averaging 5 locations is not the same as a global average. Nonetheless, we digitised the same figure and found that $H^{cp} = 3.3 \times 10^4$ M atm^{-1} corresponded to a wet deposition lifetime of 80–300 hours (average = 190 hours ≈ 8 days). To also consider the dry deposition contribution, we use results from Safieddine et al.[11] who found that for species with similar H^{cp} (e.g., glycoaldehyde, $H^{cp} = 4.2 \times 10^4$ M atm^{-1}), wet deposition accounted for roughly two thirds of total deposition. This would decrease the lifetime against deposition to $\tau_{dep} \approx 5.5$ days. Combining this estimate with a chemical removal lifetime due to OH of 20 days and due to photolysis of 7 days (the assumptions provided in SANF25), it is possible to compare the fate of CF_3CHO with the assumptions in SANF25, versus the values we reported in PP23, as shown in Table 1.

Our upper range from PP23, reproduced in Table 1, is similar to the fraction proposed by SANF25. Why, then, is the PP23 fraction close to SANF25 with such different H^{cp} values? We identify four factors:

(1) Deposition velocity is a highly non-linear function of H^{cp}.

(2) We modelled a higher $V_{dep} = 0.21$ cm s^{-1} than derived directly from H^{cp}. This is equivalent to modelling H^{cp} in the range 100 to 1000 M atm^{-1}.

(3) Dry deposition is much less dependent on H^{cp} than wet deposition. For example, Bi and Isaacman-VanWertz[10] (Fig. 5)

Table 1 Comparison of the percentage contribution of each loss process to total atmospheric removal of CF$_3$CHO as estimated in SANF25 (based on relative lifetimes) and modelled in PP23 (using AtChem2 forced with different V_{dep} values)[a]

Fate	SANF25 (τ_{dep} = 5.5 days)	PP23 C15_lqy_ldep (V_{dep} = 0.21 cm s^{-1})	PP23 G15_lqy_udep (V_{dep} = 0.08 cm s^{-1})	PP23 G15_lqy_ldep (V_{dep} = 0.02 cm s^{-1})
OH reaction	13%	11%	15%	17%
Photolysis	38%	48%	64%	75%
Deposition	49%	41%	21%	7%

[a] From Fig. 5a–c in PP23.

shows that dry deposition changes by about 8-fold for H^{cp} changing from 10 to 10^5 M atm^{-1} whereas wet deposition changes by 1000-fold. Examination of the values in Table 1 of Safieddine et al.[11] provides a similar conclusion. In PP23, we included global averaging of both wet and dry deposition to determine V_{dep}, thereby reducing the impact of a lower H^{cp}.

(4) We suspect that a simple lifetime-based estimate may overestimate the role of wet deposition. SANF25 calculate that the lifetime against wet deposition would be more than 11 years at H^{cp} = 13 M atm^{-1}. But at H^{cp} = 0.96 and 13 M atm^{-1} (the right two columns in Table 1, and Fig. 5 of PP23), our modelling showed deposition accounted for 7–21% of CF$_3$CHO loss, with wet deposition between 8% and 12% of the depositional loss (Table 2 in PP23). In neither scenario is this pathway insignificant.

The final consideration is what a higher deposition rate would mean for the HFC-23 growth rate. While we did not model HFC-23 growth rate in a scenario using V_{dep} = 0.21 cm s^{-1} in PP23, we can estimate the impact by combining and extrapolating the results from Table 1 in this work and Table 5 in PP23. We found in PP23 that increasing V_{dep} from our lower value (G15_lqy_ldep scenario) to our upper global value (G15_lqy_udep scenario) increased the deposition contribution by a factor of ~3, which decreased the HFC-23 growth rate by ~15%. Table 1 shows that a further increase from our upper global value (G15_lqy_udep scenario) to our maximum value (C15_lqy_ldep scenario) increased the deposition contribution by a factor of ~2, while using the lifetime-based estimate would increase the deposition contribution by a factor of ~2.3. Extrapolating from the results at the lower V_{dep} implies a 10–12% decrease in HFC-23 growth rate associated with the doubling of the deposition contribution. In other words, we would expect that at higher V_{dep} values (consistent with much higher H^{cp}) and our lower ϕ(CHF$_3$) value, the HFC-23 growth rate would decrease from 0.038 to ~0.033 ppt per year in the 2015 emissions scenario and from 0.37 to 0.33 ppt per year in the 2050 emissions scenario. This impact remains inconsequential compared to the uncertainties that we have acknowledged in the model and the unmeasured CF$_3$CHO physical properties.

4. Conclusions

To return to the conclusions posited in SANF25:

(i) The quantum yield for photolysis of CF$_3$CHO to form CHF$_3$ remains a matter of community debate. We assert that ϕ(CHF$_3$) = 0.01 is a reasonable upper limit for our modelling, and ϕ(CHF$_3$) = 0.003 a reasonable value to use to test model sensitivity (noting that we did not consider this a lower limit, simply the lower of two plausible test values). This assertion is reinforced by reports published after PP23 showing quantum yields in this order of magnitude at atmospherically relevant pressures, and even higher at shorter wavelengths. Given the uncertainty at the time of PP23 publication, ϕ(CHF$_3$) = (0.003, 0.01) were reasonable values to test in our suite of box model simulations. An important result highlighted in PP23 is that the atmospheric yield of CHF$_3$ is directly proportional to ϕ(CHF$_3$) used in the model, so that other scientists can scale our results by whatever ϕ(CHF$_3$) future studies determine.

(ii) In the case of deposition, in PP23 we modelled a range of scenarios, including higher deposition velocities equivalent to H^{cp} ≈ 100–1000 M atm^{-1} that represented both wet and dry deposition. The maximum estimated fraction for deposition of CF$_3$CHO in PP23 is 41%, compared to the 49% estimated using the lifetimes posited in the SANF25 comment. Extrapolating the resultant change in the HFC-23 growth rate implies a decrease of 10–12% relative to the values published in PP23, well within the uncertainties in the estimates of the CF$_3$CHO physical properties. Given the non-linearities in the relationships between H^{cp}, V_{dep}, CF$_3$CHO fate, and HFC-23 production, piecing apart the true implications of a higher H^{cp} will require implementation in atmospheric models.

The chemistry of HFOs and CF$_3$CHO is an active area of current research. Several more papers have been published since PP23, including reports of reaction of HFOs with O$_3$[13] and of CF$_3$CHO reacting with HO$_2$,[12] as well as the quantum yield reports mentioned above. Atmospheric hydration of CF$_3$CHO and the fate of the hydrate formed, while interesting, is out of scope of the PP23 paper, and deserves a proper scientific investigation to add to this ongoing body of work.

In summary, we believe that both reports summarise the situation nicely:

● PP23: "… the true strength of this sink remains uncertain. We emphasize the need for measurements of CF$_3$CHO physical properties in future studies."

● SANF25: "Experimental data on K_{hyd} and H* for CF$_3$CHO are urgently needed to settle some of these questions. Then further modelling with revised input parameters is warranted."

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What is needed now is for the atmospheric chemistry measurement and modelling communities to determine the physical properties of CF$_3$CHO, refine the photochemical mechanisms, and implement newly discovered chemistry and processes into models. Our future work will use a range of parameters in a more sophisticated model than we used in PP23 to attempt to better constrain these relationships. We welcome further modelling efforts from other groups to move the scientific conversation forward.

Data availability

No primary research results, software or code have been included in this work and no new data were generated or analysed as part of this reply.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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