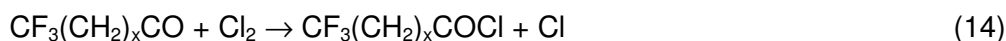


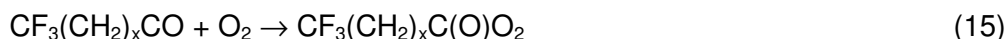
We greatly appreciate the referee's comments on our manuscript entitled "Tropospheric photooxidation of CF₃CH₂CHO and CF₃(CH₂)₂CHO initiated by Cl atoms and OH radicals", by M. Antiñolo, E. Jiménez, A. Notario, E. Martínez, and J. Albaladejo.

1) Comment on the possible Cl atom regeneration

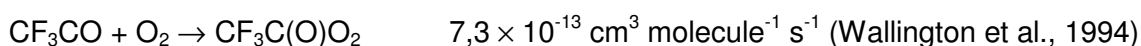
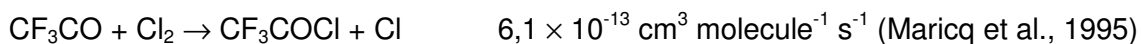
As stated on Page 24792 of the manuscript the Cl decay profiles were observed to be biexponential after photolysis of Cl₂/aldehyde mixtures. Similarly to other Cl-reactions where Cl₂ was used as a Cl photochemical precursor, the chlorine atom regeneration could be explained by the reaction of CF₃(CH₂)_xCO radicals with Cl₂:



After adding O₂ as a radical scavenger, the Cl decay profiles became monoexponential, indicating the predominance of reaction (15) versus reaction (14):



As stated on Page 24792 of the manuscript no kinetic data on the reactions (14) and (15) are available in the bibliography. Therefore in this work the kinetic behaviour of CF₃(CH₂)_xCO radicals was assumed to be similar to that of CF₃CO radicals (smallest fluorinated radical of the series, x = 0) rather than CH₃CO radicals used by the reviewer. In this way, the deactivating effect CF₃ group is included in the estimation. Of course, the effect of the methylene groups (when x = 1 and 2) on $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{O}_2)}$ and $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{Cl}_2)}$ is not known, but it would be expected an increase in both rate coefficients. Again, the magnitude of such an increment is not known.



Thus, as an approach we assumed $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{O}_2)} / k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{Cl}_2)} = k_{(\text{CF}_3\text{CO} + \text{O}_2)} / k_{(\text{CF}_3\text{CO} + \text{Cl}_2)} = 1.2$. The worst scenario corresponds to a low O₂ concentration and high Cl₂ concentration, what is presented on Page 24792 of the discussion paper ([O₂]₀ / [Cl₂]₀ = 50. However, the highest [O₂]₀ / [Cl₂]₀ ratio employed was up to ca. 70. Considering these concentration ratios and $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{O}_2)} / k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{Cl}_2)}$, the rate

ratio $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{O}_2)}[\text{O}_2] / k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{Cl}_2)}[\text{Cl}_2]$ would range from 60 to 84. In other words, about 98% of $\text{CF}_3(\text{CH}_2)_x\text{CO}$ would react with O_2 and only 2% of those radicals would regenerate Cl atoms. Further, and as can be seen in Figure A, Cl temporal profiles (in log scale) are linear over usually two lifetimes, indicating that the Cl regeneration has been minimized as in other previous works. Therefore, Cl-regeneration can be considered negligible under our experimental conditions.

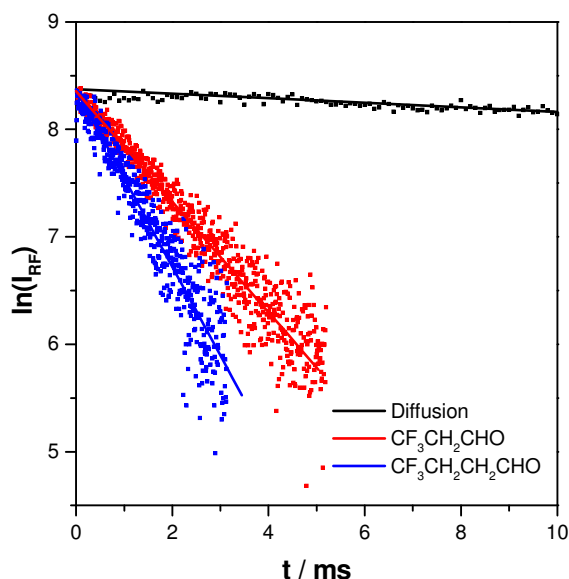


Figure A. Decay temporal profile of RF signal of chlorine atoms recorded at 100 Torr and 331 K for $\text{CF}_3\text{CH}_2\text{CHO}$ and 351 K for $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHO}$.

As suggested by Referee #1, some examples of the Cl temporal profiles could be included in the revised manuscript or in the supplementary information.

Effect of temperature in the possible Cl-regeneration

Referee #1 suggests that Cl atoms could regenerate faster at high temperatures if the activation energies of the reaction of CH_3CO radicals with O_2 ($E_a = 0$) and Cl_2 ($E_a/R = 47$ K, Tyndall et al. (1997)) are taken into account. The reaction of CH_3CO with Cl_2 was studied at temperatures below 298 K (298-228 K). If we extrapolate those results at $T > 298$ K, the rate coefficient $k_{(\text{CH}_3\text{CO} + \text{Cl}_2)}$ at the highest temperature ($T = 371$ K) is $2.47 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, implying an increase of 0.3% in the

possible Cl regeneration. So, under these “speculative” conditions, the Cl regeneration would be within the experimental uncertainties.

Again, the magnitude of the effect of temperature on $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{O}_2)}$ and $k_{(\text{CF}_3(\text{CH}_2)_x\text{CO} + \text{Cl}_2)}$ is not known and further studies on these reactions at 298 K and above would be helpful. However, the experimental decay profiles obtained for Cl atoms at high temperatures (see Figure A) show that there is no appreciable Cl-regeneration.

Effect of addition of different O₂ concentrations

The following statement on Page 24792 of the discussion paper is not precise enough and it will be changed in the revised manuscript: “A few experiments were performed with $[\text{O}_2] \sim 2 \times 10^{16}$ molecule cm^{-3} for a limited range of aldehyde concentrations, and the obtained rate coefficients were similar to those obtained with $[\text{O}_2] \sim 1 \times 10^{16}$ molecule cm^{-3} ”. Despite the reduction of the signal-to-noise ratio, the initial $[\text{O}_2]$ was set between 1.0 and 2.5×10^{16} molecule cm^{-3} over the T-range studied in order to ensure the minimization of Cl atom regeneration. For example, in Table A the values of k_{Cl} at room temperature and at different pressures, were listed together with the initial O₂ concentration used in the experiments. Likewise, no difference on k_{Cl} outside the error limits was observed at 298 K and other temperatures, as observed in Table B.

Table A. Rate coefficients k_{Cl} for $\text{CF}_3\text{CH}_2\text{CHO}$ and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHO}$ at 298 K and as a function of total pressure.

p / Torr	$[\text{O}_2] \times 10^{-16} /$ molecule cm^{-3}	$(k_{\text{Cl}} \pm 2\sigma) \times 10^{11} / \text{cm}^3$ molecule ⁻¹ s ⁻¹	$[\text{O}_2] \times 10^{-16} /$ molecule cm^{-3}	$(k_{\text{Cl}} \pm 2\sigma) \times 10^{11} / \text{cm}^3$ molecule ⁻¹ s ⁻¹
CF ₃ CH ₂ CHO			CF ₃ CH ₂ CH ₂ CHO	
50	1.6	1.52±0.07	1.5	3.34±0.19
100	1.7	1.53±0.06	1.7	3.41±0.79
150	1.9	1.60±0.06	1.9	3.24±0.53
200	2.1	1.48±0.06	2.2	4.00±0.22

Table B. Rate coefficients k_{Cl} for CF_3CH_2CHO as a function of temperature.

T / K	$[Cl_2] \times 10^{-14} /$ cm^{-3}	$[Cl]_0 \times 10^{-11} /$ cm^{-3}	$[RCHO] \times 10^{-13} /$ cm^{-3}	$[O_2] \times 10^{-16} /$ cm^{-3}	$(k_{Cl} \pm 2\sigma) \times 10^{11} /$ $cm^3 \text{ molecule}^{-1} s^{-1}$
268	3.7	4.3	0.92-8.0	1.7-2.5	1.37±0.10
278	3.2	4.6	0.80-7.5	1.8-1.9	1.42±0.10
288	2.9	4.0	0.79-7.7	1.6-1.9	1.38±0.11
298	3.2	4.5	0.39-15	1.5-2.2	1.55±0.22
316	2.5	3.8	1.8-17	1.3-1.5	1.67±0.38
331	2.4	3.6	1.6-15	1.5-1.2	1.75±0.32
351	2.2	3.4	1.8-12	1.3-1.1	1.80±0.36
371	2.2	3.4	1.4-13	1.0-1.7	1.84±0.15

Table C. Rate coefficients k_{Cl} for $CF_3CH_2CH_2CHO$ as a function of temperature.

T / K	$[Cl_2] \times 10^{-14} /$ cm^{-3}	$[Cl]_0 \times 10^{-11} /$ cm^{-3}	$[RCHO] \times 10^{-13} /$ cm^{-3}	$[O_2] \times 10^{-16} /$ cm^{-3}	$(k_{Cl} \pm 2\sigma) \times 10^{11} /$ $cm^3 \text{ molecule}^{-1} s^{-1}$
268	3.1	3.8	1.3-11	1.6-2.2	2.85±0.45
278	2.9	3.6	1.5-13	1.6-1.8	2.98±0.20
288	2.7	3.7	1.3-11	1.5-1.9	3.20±0.14
298	3.0	4.1	0.75-21	1.4-2.2	3.39±0.70
316	2.4	3.6	1.2-11	1.3-1.5	4.05±0.46
331	2.3	3.3	1.2-10	1.3	4.60±0.24
351	2.3	2.8	1.3-11	1.2-2.3	4.79±0.74
371	2.1	2.6	1.2-10	1.0-1.4	5.13±0.41

2) Minor Comments

We agree with the reviewer that the statement on Page 24875 of the paper under discussion is too broad. The global warming potentials of HFCs range from 53 (HFC-152, $\tau = 0.6$ yr) to 14,760 (HFC-23, $\tau = 270$ yr) over an integration time horizon of 100 years (WMO, 2006). Generally, the higher the atmospheric lifetime for a HFC is, the higher its GWP will be. Of course, the radiative efficiency ($W m^{-2} ppbv^{-1}$) of HFCs is a determining factor in GWP (as it can be seen in Table D).

Thus, the statement on Page 24875 of the discussion paper will be changed by “Moreover, both of them (referring to HCFCs and HFCs) are in general very strong greenhouse gases with high Global Warming Potentials (GWP) commonly associated with long tropospheric lifetimes and strong absorption in the IR region”.

Table D.

	Radiative efficiency	tau	GWP (100-yr)
HFC-23	0.19	270	14,760
HFC-32	0.11	4.9	675
HFC-41	0.02	2.4	92
HFC-125	0.23	29	3,500
HFC-134	0.18	9.6	1,100
HFC-134a	0.16	14	1,430
HFC-143	0.13	3.5	353
HFC-143a	0.13	52	4,470
HFC-152	0.09	0.6	53
HFC-152a	0.09	1.4	124
HFC-227ea	0.26	34.2	3,220
HFC-236cb	0.23	13.6	1,340
HFC-236ea	0.3	10.7	1,370
HFC-236fa	0.28	240	9,810
HFC-245ca	0.23	6.2	693
HFC-245fa	0.28	7.6	1,030
HFC-365mfc	0.21	8.6	794
HFC-43-10mee	0.4	15.9	1,640

Section 3.3. Impact of fluoroaldehyde chemistry on air quality

We agree with Referee#1 that the atmospheric abundance of fluorinated aldehydes is currently low. However, the possible widespread use of fluorinated alcohols as substitutes of HFCs will inevitably lead to an increase in fluoroaldehyde concentrations, since they are the major oxidation products. Thus, further studies on the degradation products of their homogeneous oxidation and UV photodissociation will be needed in order to evaluate the environmental impact of these fluoroaldehydes. So, the statement on Page 24798 is changed by:

“As the major degradation routes are reactions with OH radicals and UV photolysis, products of such processes should be known in order to evaluate the influence on the air quality”.