We would like to thank the reviewer for the thorough reading of the manuscript as well as for evaluating and improving our work by his/her comments. Detailed answers to his/her comments are presented below.

General comments

1. Introduction is well constructed, and the subject well presented. The objectives are clearly defined, and the method explained with details. The results are worth publishing, but I think a deeper exploration of the results can be performed. For the moment, my opinion is that the results do not entirely support the conclusions raised by the authors (see my remarks below).

Authors reply: Conclusion section has been revised and precisions are now included in the manuscript (see replies in comments 16-19)

2. I see 2 main points that can be explored by the authors to improve the paper:
- It is clearly showed in the paper that the humidity affects the sensitivity of the instrument. An interesting point discussed by the author is how humidity affect the protonation, giving about the chemical reactions that take place in a drift tube. The fragmentation is clearly discussed, but less attention is paid to clustering with H3O+. This should more extensively discussed. In addition, the sum of ions that can be attributed to one species (its fingerprint on the mass spectra) must be investigated, to see if their sum is constant with humidity. The effect of the normalization by primary ions (including water clusters) as frequently performed for PTRMS sometimes help to reduce the effect of humidity. This must be investigated and further discussed.

Authors reply: Initially we would like to note that our study was focused on the masses formed from the primary ions. As the SIFT-MS is a quadrupole mass spectrometer, a particular group of masses were followed. However, based on our experimental observations and literature, useful conclusions can be drawn.
In case of formaldehyde we provide a detailed discussion in the initial version of the manuscript about the role of water clustering under SC and CC (section "Ion Chemistry Involved in Formaldehyde Measurement with H_3O^+ Precursor Ion"). Under SC the sensitivity of the instrument is independent on RH therefore the possible contribution of the 1st water cluster ($H_2O \bullet H_3O^+$) to the sensitivity of the instrument is negligible. Under CC of SIFT-MS, we have clearly stated in the manuscript (in revised version lines 445-446) that for ratio I_{37}/I_{19} greater than 0.55, the effect of water clustering could play a role: "However, in case of CC where the I_{37}/I_{19} is greater than 0.55, the gradual reduction in FM sensitivity could be due to the competition between (R2a) and (R3a)." Attempting to shed more light on the contribution of water clustering to the detection of formaldehyde under CC of the SIFT-MS, the comparison of calibration factors with I_{37}/I_{19} ratio can provide insights. In particular, comparing the calibration factor of the instrument under dry (I_{37}/I_{19} = 0.005) and 30% RH, where I_{37}/I_{19} = 0.56, we note that it remains almost stable. In other words, an increase of 112 times in the relative abundance of the 1st water cluster compared to H_3O^+ has no impact on SIFT-MS sensitivity at the mass 31. However, above that threshold, an increase of 44% in the relative contribution of the 1st water cluster, causes a decrease of 44% in the sensitivity of the instrument at mass 31, i.e. linear drop. In case water clustering was playing a major role, then we would anticipate its contribution to be more visible from dry to 30% of RH due to the intense increase of its relative abundance.
Furthermore, in the wrap up section (in revised version lines 478-481) there is also a relevant comment about the possible contribution of water clustering: "This behaviour contrasts with PTR-MS. (R3) and (R4), involving PMH production and inducing a lower sensitivity at the mass peak 31, seem to be of minor importance or at least to be in equilibrium state for I_{37}/I_{19} below 0.55. Above that threshold,

their occurrence could explain a lower sensitivity but this point needs further investigations to be experimentally validated."

In the case of glyoxal, we provide a detailed discussion about the sensitivity loss of the instrument (in revised version lines 517-539) which under our conditions is mainly attributed to competition of protonation and deprotonization reactions (reactions 5a and b). **However, to address the reviewer comment a new series of experiments were carried out collecting the complete mass spectrum of glyoxal under dry, 10%, 30%, 50% and 70% of RH under SC and CC.** The mass spectra were collected under a steady state concentration of GL at 300 ppb. The normalized mass spectra recorded under dry and 50% of RH under CC conditions (where water clustering is anticipated to be more important) are now included in the updated version of the supplementary material (see also below) and a relevant discussion about the effect of water clustering is now presented in the revised version of the manuscript (lines 578-593, and 704-705). The normalization was performed at the highest mass peak observed at each RH.

Under dry conditions the main peak observed is the m/z =59. The intensity of the m/z =77 ($C_2H_2O_2^+·H_2O$) that correspond to the peak originating from the reaction of GL with the 1st water cluster ($H_2O.H_3O^+$) **corresponds solely to 1%** of the peak 59. The intensity of the m/z =31 that corresponds to the fragmentation of GL is 15% of the peak 59. Under 50% of RH the intensity of the mass peak 59 is diminished and the primary peak in the mass spectrum is the one with the mass 31. **Interestingly, the mass peak 77 is not impacted by RH and has a similar absolute intensity with dry. Therefore, our results clearly demonstrated that the decrease of the instrument sensitivity in the mass 59 with increasing RH is due to the fragmentation of GL and the impact of water clustering is negligible in our SIFT-MS.**

mass spectra based on H_3O^+ m/z = 19 (CC)
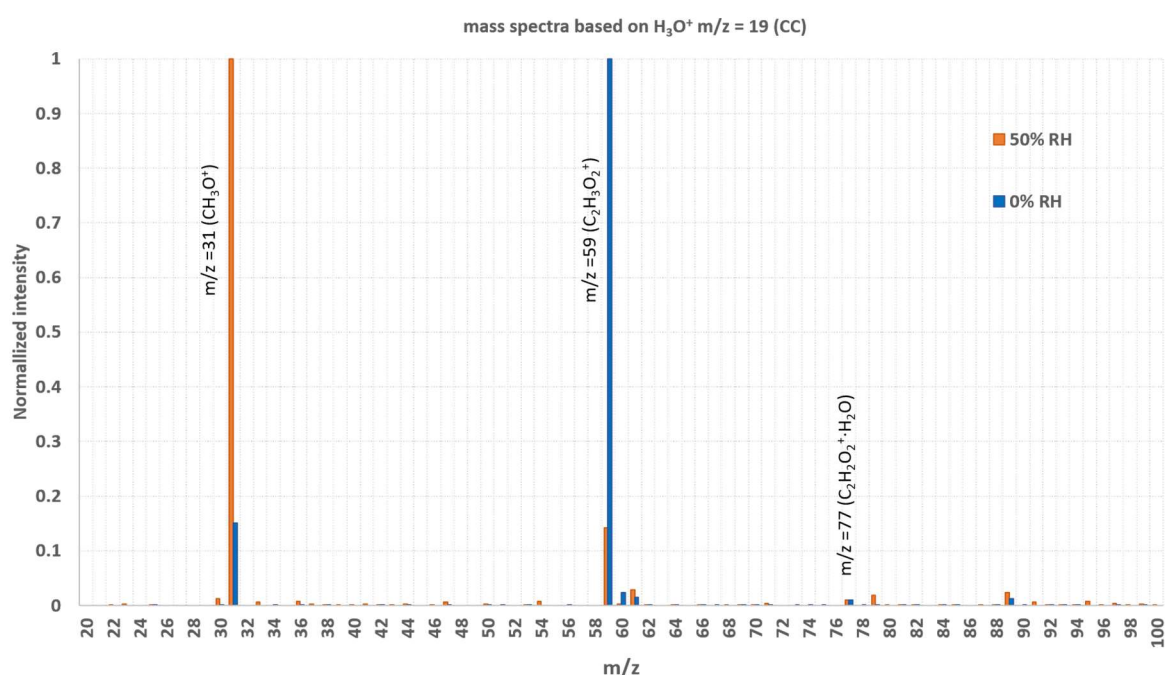
3. The sensitivity of the SIFT MS to formaldehyde or glyoxal shows a nice relation with I37/I19, which traduces the ambient humidity variations. A proposition of a correction factor, in other words a formula to calculate the sensitivity as a function of this ratio can be obtained from these experiments to be used for monitoring studies. I suggest that the authors estimate the correct formula and discuss its use. This

would improve the output of the paper and make a new step forward to ambient measurement of glyoxal and formaldehyde.

Authors reply: In case of **glyoxal**, the sensitivity of the instrument versus I_{37}/I_{19} is already plotted in figure 5 and the corresponding formula is presented in the figure caption. Nevertheless, as correctly pointed by reviewer, in order to emphasize its application for monitoring studies, we have modified the manuscript text (added lines 521-525).

Lines 521-525: The calibration factors were fitted versus the I_{37}/I_{19} ratios and the sensitivity of the instrument under SC and CC are given by the following expression:

$$C_F^{59}(counts\ ppb^{-1}) = \frac{a}{b+\left(\frac{I_{37}}{I_{19}}\right)^c}\ \text{Eq. (5)}$$

where a=2.99, b=0.04, c=1.20 for SC and a=4.53, b=0.03, c=1.74 for CC, respectively.

In the case of **formaldehyde** and SC no RH dependence was noticed (considering the experimental uncertainties). However, under CC there is an RH dependence and, following the reviewer's suggestion we plotted the experimental results (a new figure was added in the supporting information material, Figure S2) and now we provide the corresponding formula in the main manuscript. Modifications were performed in lines 353-358 and now the text reads:

Lines 353-358: Under CC, to express the relative humidity dependence of the instrument sensitivity at the mass peak 31, the calibration factors were plotted as a function of the I_{37}/I_{19} ratio, using a weighted fit power function (Fig. S2). The weighted fitting considers the uncertainties denoted for each calibration factor. The following expression describes the instrument sensitivity under SC for the mass peak 31:

$$C_F^{31}(counts\ ppb^{-1}) = 162 - 82.3 \left(\frac{I_{37}}{I_{19}}\right)^{2.41}\ \text{Eq. (4)}$$

4. My recommendation is that the paper should published only after the authors addressed the points raised here.

Authors reply: We have tried to address all reviewer's comments, employing a series of new experiments, providing clarifications and text modifications to improve the quality of the manuscript.

Specific Comments

5. Is the ap2e ProCeas calibrated? Did the authors regularly check the blanks/background of the instrument? As this instrument is used as a reference to evaluate the sensitivity of the SIFT-MS, that is necessary. In addition, why not using the theoretical concentration based on dilution calculation to evaluate the SIFT sensitivity? As the concentrations in the standards are known and the flows are controlled by MFC, the theoretical concentration in the lines can be easily calculated.

Authors reply: The ap2e ProCeas analyzer determines the concentration of formaldehyde in the air flow using a multipath IR spectrometer. Under a constant optical length and knowing the absorption cross section of formaldehyde, and the application of Beer Lambert law, the concentration of formaldehyde

is determined. Therefore, calibration is not necessary considering a stable pathlength, which is continuously measured by the instrument. Nevertheless, in all experiments, the concentration of formaldehyde in the gas flow has also been calculated based on the cylinder concentrations and the flow rates (method proposed by the reviewer, was used for the calculation of glyoxal concentration) and was compared with the analyzer response for cross validation purposes. In all cases the differences between formaldehyde concentrations estimated from the measured flow rates and the analyzer were below 4%, varying randomly without any systematic trend. However, in the case of formaldehyde, which is a sticky compound and possible losses on the Teflon lines could impact the concentration levels estimated based on flow rates, we decided to use the concentrations of formaldehyde analyzer which was placed close to SIFT-MS instrument. Concerning the blanks/backgrounds of the instrument, they were checked before and after each experiment using dry or humid zero air.

6. A long path FTIR is used for several occasion in the experiments performed by the authors. Please provide at least a brief description of the instrument.

Authors reply: Following the reviewer's comment a paragraph is included in the section 2.2 Experimental Setup for the description of the instrument. (added lines 215-221)

7. L.232-233: "m/z =59 (C2H3O2$^+$) and m/z=88 (C2H2O2NO+), originating from H3O+ and NO+ respectively are used." Why only these two ions are used? Are other potential ions (fragments, clusters, …) investigated?

Authors reply: Our study was mainly focused on the primary mass peaks of glyoxal formed from H_3O^+ and NO^+ ions, while O_2^+ ion was checked and finally not considered in the present study, due to significant fragmentation and low sensitivity strongly impacted by RH (lines 493-495). Regarding H_3O^+ the fragmentation of GL has already been discussed in details in the manuscript. Furthermore, the new experiments performed (see also comment 2) evidenced that the formation of other peaks due to water clustering was negligible. Therefore, in case of H_3O^+ only the mass peaks 59 and 31 are of importance and they have been already discussed in the manuscript. **In case of NO$^+$ we have also collected the complete pattern and we have solely observed the mass peak 88.** No fragmentation or second water clustering was observed. The formation of $NO^+\bullet H_2O$ cluster (m/z=48) was observed during our experiments increasing the RH, but its relative abundance was always below (0.45% of that of NO^+). The $NO^+\bullet H_2O$ cluster could react with GL according to reaction 10. Michel et al., have shown that the reaction of VOCs with the $NO^+\bullet H_2O$ clusters results to H_2O elimination and the formation of $VOC\bullet NO^+$.

8. L.250-291: This part is not results and discussion but rather material and methods. Please move this part to the appropriate section in the manuscript

Authors reply: We consider the optimization of the operational conditions part of the results of the current study. In addition, the strategy followed to improve the method and the performance of the instrument constitute part of the discussion. Therefore, we prefer to keep it in the results section. Besides the flow of the article is not impacted by the presence of this section.

9. L.325: "The background [H2O] has been estimated in the range of 10^{10} molecule cm-3". I do not see an explanation about how background [H2O] is calculated/measured.

Authors reply: The background H_2O concentration is estimated based on H_2O residual levels in the zero-air flow, i.e. < 2ppm corresponding to RH <0.01%. The expression used to make the calculation is given in the caption of table 1.

10. L.342-343: "sensitivity is not impacted by water presence when the relative ratio of I37/I19 is below ca. 0.55, irrespectively of the SIFT-MS operation mode." This is of great importance, because it implies that in CC, the ambient humidity will affect the sensitivity when RH is above 30 %, which almost always the case. So, unless a correction as a function of humidity is applied, CC cannot be used for ambient measurement of FM in H3O+ mode.

Authors reply: Indeed, the operation of the instrument under CC revealed a reduction to SIFT-MS sensitivity for RH levels above 30%. Following the suggestion of the reviewer in comment 3, in the revised version of the manuscript we plotted the calibration factors as a function of I_{37}/I_{19} ratios (similar approach was used in case of GL). Applying this expression, the concentrations of FM can be retrieved even under environments where the RH changes during the experiment by simply following the I_{37}/I_{19} ratio.

11. Section 3.1 In this section, the authors discussed the primary ions and the first water cluster under SC and CC. In the CC, the pressure is higher, with a lower residence time. I am thus wondering whether the 2nd water cluster (H2O.H2O.H3O+) behave in this condition? Can it be important? Should it be considered? In addition, the figure S1 shows that there are more water clusters that H3O+ at 70 %. What can be the implication? Are these operating conditions valuable for humidity higher than 70 %, where the water cluster will be even more important?

Authors reply: Under custom operational conditions, not only the pressure increase (as correctly pointed by reviewer) but also the temperature decrease in the flow tube, enhance the relative abundance of the first ($H_2O.H_3O^+$ m/z = 37) and the second ($H_2O.H_2O.H_3O^+$ m/z = 55) water clusters compared to standard operational conditions. In the following table we present the absolute intensities of the H_3O^+ and the first two water clusters under standard and custom operational conditions. Under standard conditions the absolute intensity of the 2nd water cluster is always below 2% of the primary H_3O^+. Under custom conditions the 2nd water cluster becomes important for RH above 30% and under 70% of RH has an equal intensity with the H_3O^+ and the 1st water cluster. However as noted in comment 2 the effect of water clustering has a small impact in the sensitivity of the instrument of formaldehyde while in case of glyoxal the fragmentation is the primary reason of the sensitivity loss and not the formation of GL-water clusters.

m/z	Standard conditions			Custom conditions		
	19 (H_3O^+)	37 $(H_2O.H_3O^+)$	55 $(H_2O.H_2O.H_3O^+)$	19 (H_3O^+)	37 $(H_2O.H_3O^+)$	55 $(H_2O.H_2O.H_3O^+)$
Dry	3.1×10^6	0.03×10^5	44.5	2.2×10^6	0.1×10^5	130
10% RH	2.8×10^6	2.5×10^5	0.1×10^4	2.0×10^6	5.6×10^5	0.9×10^5
30% RH	2.7×10^6	7.2×10^5	0.9×10^4	1.8×10^6	10.1×10^5	4.3×10^5
50% RH	2.7×10^6	11.1×10^5	2.9×10^4	1.5×10^6	11.9×10^5	8.8×10^5
70% RH	2.4×10^6	13.0×10^5	5.2×10^4	1.3×10^6	13.0×10^5	13.0×10^5

12. It would also be interesting to comment (even briefly) about other possible clusters from NO+ and O2+ ionization, and the whether the increasing pressure in the reactor increase the level of impurities that may arise from the source.

Authors reply: The monitoring of formaldehyde and glyoxal was achieved following only the mass peaks formed from the primary ions. As discussed in the manuscript and previously in comment 7, we were focused on the chemistry of H_3O^+ and NO^+ ions, while O_2^+ ion was checked and finally excluded because of the important fragmentation peak appearance, and strong impacts by RH.

In the case of FM, we have not observed any peak with NO^+ and thus we do not anticipate the formation of other peaks from NO^+ clustering. In case of Glyoxal, as already mentioned and discussed in the manuscript and as evidenced in the new series of experiments (comment 7) we solely observed the mass peak 88, which was slightly increased with the RH. This was attributed to the formation of $NO^+•H_2O$ cluster (m/z=48) according to reaction 10. Our observations are in accordance with literature where it has been shown that the reaction of VOCs with the $NO^+•H_2O$ clusters results to H_2O elimination and the formation of $VOC•NO^+$ (Michel et al., 2005).

The increase in flow tube pressure raises slightly the background of the instrument for the main mass peaks used to monitor the VOCs, however it resulted to a much higher sensitivity (as discussed in the article). In general, the increase of pressure increased the signal to noise ratio which resulted to higher instrument sensitivity.

13. L.428-428: "under SC the calibration factor at m/z 31 remains constant within the experimental uncertainties, and thus (R3) seems to have insignificant impact on the sensitivity of the instrument" This sentence is true considering the uncertainty at 70 %, but it seems that higher RH will decrease (maybe a little) the sensitivity. I think that it should be noticed, or at least please precise that your sentence is true only for RH between 0 and 70 %, and for higher humidity more experiments would be needed.

Authors reply: Precisions have been added in the text according to reviewer's suggestion (in revised version lines 442-445). Now the text reads: "**However, as abovementioned, under SC the calibration factor at m/z 31 remains constant within the experimental uncertainties and the RH range studied (0 - 70 %), and thus (R3) seems to have insignificant impact on the sensitivity of the instrument."**

14. Figure 6: This figure is interesting and shows that the effect of RH is not really a decreasing sensitivity but rather a change in distribution of ions, due to several reactions that occurred in the drift/reaction tube such as protonation, charge transfer, fragmentation, or clustering. The figure 6 only shows the fragmentation for glyoxal, which is already interesting. But it would be necessary to show other ions such as water clusters. Finally, it raises the following question: are VOC.H+ ions the most appropriate ones to monitor formaldehyde and glyoxal in ambient air (or in humid conditions in the lab)?

Authors reply: The effect of water clustering has been discussed in comment 2 and a relevant text has been added in the manuscript. **Our results clearly demonstrated that the decrease of the instrument sensitivity in the mass 59 with increasing RH is due to the fragmentation of GL and the impact of water clustering is negligible in our SIFT-MS.**

Concerning the last part of reviewer's comment "Finally, it raises the following question: are VOC.H+ ions the most appropriate ones to monitor formaldehyde and glyoxal in ambient air (or in humid conditions in the lab)", authors think that it is appropriate. This is also discussed in the conclusion section of the manuscript. For instance, in case of formaldehyde and standard operational conditions, the

instrument sensitivity and stability with RH clearly demonstrate that SIFT-MS and the H_3O^+ ion can be used for its detection. In case of glyoxal, this is also feasible. As clearly shown in Figure 5, the fitting of calibration factors with I_{37}/I_{19} ratio is feasible and thus the concentrations of glyoxal can be retrieved even under environments where the RH changes during the experiment by simply following the mass peak 59 and the I_{37}/I_{19} ratio. To conclude, authors think that the $VOCH^+$ ions are still appropriate for the monitoring of these species. Nevertheless, if with this comment the reviewer implies that the use of NO^+ ion could potentially be an alternative way for RH studies and especially for the case of glyoxal, then yes, we acknowledge this interesting thought, but more work should be done to improve instrument sensitivity with NO^+ ion.

15. L. 610-612: Again, this shows that in real ambient conditions where RH is always higher than 10 %, that GL.H+ might not be the main ion formed in the drift, so maybe not the good one to follow if one wants to measure glyoxal

Authors reply: We have provided relevant discussions in comments 2 and 14 about the relevance of using H_3O^+ ion for the detection of glyoxal.

16. L. 676-677: I do not agree with the authors. The sensitivity shows a strong dependance on humidity, except for GL when NO+ is used as primary ion, where only a small change is observed. Thus, it cannot be concluded that the instrument is stable as function of relative humidity.

Authors reply: Our comment on the stability of the instrument with RH concerned the molecule of formaldehyde. This was mentioned in the initial version of the manuscript. In the revised version we modified the text providing more clarifications to avoid any confusion (in revised version lines 708-712). The text now reads: "**Remarkably, under SC the sensitivity of the instrument is not impacted by RH with a corresponding detection limit of ca. 500 ppt. Operating the instrument under CC increased the sensitivity however, for I_{37}/I_{19} above 0.58 the sensitivity is reduced and a correction factor should be applied. We recommend the operation of SIFT-MS under SC for the measurement of ambient FM greater than 500 ppt.**"

17. L. 689-690: Because of the humidity dependence of the sensitivity, I am not convinced that it is suitable for indoor, where humidity can change depending on activities (for example, window opening, cooking, etc.). In my opinion, the only conditions suitable are lab experiment at controlled humidity.

Authors reply: The reviewer is correct. The detection of GL using the H_3O^+ ion is challenging, and the reduced sensitivity with RH can make the application of SIFT-MS for GL detection in ambient air more complex but still feasible. Indeed, indoor activities such as windows opening or cooking can indeed impact the relative humidity levels. However, we would like to clarify that as clearly shown in Figure 5, the fitting of calibration factors with I_{37}/I_{19} ratio is feasible (see figure 5 caption) and thus the concentrations of glyoxal can be retrieved even under environments where the RH changes during the experiment by simply following the I_{37}/I_{19} ratio. Therefore, the major limitation is the instrument sensitivity and not the variation of the RH of the ambient environment. For that reason, we modified the text providing clarifications (in revised version lines 722-730). In the updated version the text is: "**Based on the detection limits achieved with the H_3O^+ ion, we suggest that SIFT-MS is not relevant to monitor GL in outdoor ambient air due to the strong impact of RH on SIFT-MS sensitivity. However, it should be clarified that as shown in Figure 5, the fitting of calibration factors with I_{37}/I_{19} ratio is feasible (see figure 5 caption) and thus the concentrations of glyoxal can be retrieved even under environments where the RH changes during the experiment by following the I_{37}/I_{19} ratio. Therefore, the major limitation is the instrument sensitivity and not the variation of the RH of the ambient environment. On**

the contrary, SIFT-MS can be deployed efficiently in laboratory scale studies (i.e. atmospheric simulation chambers, photochemical reactors) or indoor experimental rooms and environments where GL concentrations are in the ppb range."

18. L. 693-695: In my opinion, the sensitivity (several ppbs) in the NO+ ionization does not make it suitable for **ambient** monitoring, where low levels can be encountered.

Authors reply: There is probably a misunderstanding here. Indeed, the sensitivity levels achieved with SIFT-MS and NO$^+$ ion does not make it suitable for ambient monitoring. The comment in the manuscript mentioned: "Certainly, our research on the NO$^+$ chemistry opens new pathways for GL quantification and detection in ambient air deploying soft ionization techniques, such as PTR-MS with NO$^+$ ion, which are generally operated at higher pressures than SIFT-MS". What we mention in the text is that the possibility of using NO$^+$ in PTR-MS studies, instruments traditionally more sensitive than SIFT-MS, could open new pathways for GL detection in ambient air.

19. Conclusion: please update the conclusion according to the remarks above.

Authors reply: Conclusion section has been revised according reviewer's comments.

Minor Comments

20. L.23: "using SIFT MS" – redundant with SIFT-MS in the line above…

Authors reply: Typo corrected. Text has been modified according to reviewer's suggestion.

21. L.24: Of course, SIFT-MS provides a nice opportunity to measure many organic gases, as demonstrated by many studies since several years. I do not the interest to place such a sentence here, as a main conclusion of the study. A sentence about what the measurement of glyoxal and formaldehyde by SIFT MS can bring to the atmospheric community (in term of monitoring, for example, to identify processes or whatever) would be much appreciated.

Authors reply: A relevant sentence has been added in the manuscript. Now the text reads "This work evidences that SIFT-MS can be considered as an efficient tool to monitor the concentration of FM and GL in laboratory experiments and potentially in indoor or outdoor environments, capable of identifying their primary emission or secondary formation through (photo)oxidation processes.". Nevertheless, authors prefer to keep in the abstract the sentence about the capability of SIFT-MS to monitor low proton transfer affinity compounds.

22. L.136: please remove i and ii. They are sub list of 2 item included in a list of i and ii. The sentence will be easier to read without this second list.

Authors reply: Text has been modified according to reviewer's suggestion.

23. Section 2.1: Here, formaldehyde and glyoxal are sometimes written in full letters, and sometimes abbreviation. Please chose one form, and keep consistency through the paper (I noted few cases later in the manuscript)

Authors reply: We thank the reviewer for pointing this inconsistency. We have looked through the manuscript and we replaced the "formaldehyde" and "glyoxal" with their abbreviations (except section titles).

24. L.141: What is the uncertainty on the formaldehyde concentration the cylinder?

Authors reply: The uncertainty given by the supplier is 5%.

25. L.168-169: Keep the same tense in the sentence

Authors reply: Corrected

26. L.177: VOCs < 0.1 ppb. I guess this is for each individual VOC, not for the sum of VOCs. This precision must be added.

Authors reply: No it is not for each VOC, but total VOCs.

27. L.194: a space is missing between 1 and ppb

Authors reply: Typo corrected.

28. L.204-205: Please indicate the temperature of the flow reactor and the sampling port.

Authors reply: Text modified indicating the temperature range of the flow tube and sampling port.