Responses to Referee #1

The manuscript describes a powerful extension and combination of existing methods by combining PFBHA derivatisation on a microfluidic device with GC-MS. The target molecules discussed in this work are glyoxal and methylglyoxal, two molecules of increasing importance. The manuscript also describes intercomparison with other techniques and shows generally good agreement with these other methods. The work pursues an important direction, as there is a strong need for new, cheaper, and easier to use techniques for measurement of these two important molecules. The method appears to have better detection limits than SPME, which represents a real advance although the time-resolution is slower than that of some of the competing, but complex, methods, e.g., CE-DOAS, BBCEAS, LPI. The subject is well suited to AMT and timely.

I however have some comments that should be addressed before publication in AMT.

I) My first comment is that some of the authors have published a manuscript in the Journal of Chromatography A (Pang et al. 2013) and that publication has a lot of overlap with the one under review here. The manuscript was available online May 8 of this year, before the manuscript discussed here was accepted for publication in AMTD. The manuscript under review here is referenced in the published one as “in press”. However, unless I missed this, the published one is not referenced as “in press” in this manuscript or mentioned. This situation is confusing and needs clarification for the following reasons: Figure 1 in this manuscript is virtually the same as the combination of figures 1 and 2 in the published work. Figure 3 in this manuscript is nearly identical to figure 5 in the published work. However, in the current paper k-2 exists. I assume the difference results from the focus on glyoxal and methylglyoxal (although both show glyoxal), but an explanation would be helpful. Figure 4 in this work is fully identical to figure 5 in the published work (copyright?). Figure 7a is virtually identical to figure 7 in the published work.

The above highlights the strong overlap between the manuscripts. The separation of material between the two manuscripts and thus the scientific focus of the manuscripts is a little unclear to me. The published one is framed as a method description and the one under review here is aimed as an intercomparison (as clearly stated in the title). However, the separation is fuzzy and important method

development aspects are not included in the published manuscript but rather in this one, e.g., temperature optimization and more, and some of the material appears in both, e.g., some of the inter comparison.

In my opinion, it would be very helpful for the reviewers if the authors provide a rational for the approach they have taken with respect to separation of material between the two manuscripts.

Response: We thank the reviewer for providing invaluable comments, which are addressed in turn below:

Firstly, we should clarify that the published paper in J Chromat. A (JCA) is actually an invited review article. The JCA paper was finalized after the paper for AMT was accepted for AMTD publication. However, it was published much quicker than we anticipated - before the AMTD paper. The focus of the JCA paper is a review of the application of chemical derivatisation methods for the quantitative detection of a wide range of gaseous carbonyl compounds.

This AMTD paper focuses specifically on the quantitative detection of GLY and MGLY by a microfluidic derivatisation technique and includes specific information on calibration of these compounds and the optimization of analytical conditions (e.g. material on specific temperature, flow rate optimization experiments for GLY and MGLY detection). The environmental chamber comparison with other techniques was employed to test/evaluate whether this microfluidic derivatisation method has potential for atmospheric measurement of these important photochemical species. The JCA review paper has now been full cited in this manuscript.

Detailed responses for the comments:

Fig. 1 is deleted from the revised manuscript and the JCA paper is cited to describe the basic layout of micro-reactor and the microfluidic lab-on-chip derivatisation analytical system.

In Fig.3 the derivatisation reactions of both glyoxal and methylglyoxal are shown. Further explanation is added in the figure caption.

Fig. 4 is deleted from the manuscript and the corresponding descriptions of the GC chromatogram and MS spectra are added in this revised manuscript, with the JCA paper cited in the description.

Fig.7 (Fig.5 in the new manuscript) has been plotted differently in light of comments made by Reviewer #2 – separate graphs for GLY and MGLY.

Section 3.2 of "Solvent Selection" is deleted and Sections 3.3 and 3.4 are merged together and abridged in length so as to avoid unnecessary repetition from what is written in the JCA article. However, we include Fig. 5 (Fig. 3 in the new manuscript) which shows method optimisation specifically for GLY and MGLY, since these species are the focus of this paper. This material is not published elsewhere.

II) A second major comment is that the manuscript could benefit from stating more clearly the suitability of the method for ambient measurements, especially for methyl glyoxal, for which there is a strong need for better field measurement methods, and clarify the comparison with other methods, especially with respect to how "rapid" the measurements are.

1. The abstract mentions MDLs but does not mention precision or accuracy of the method nor the measurement time and whether this enables field measurements. It is stated in the abstract that "These MDLs are below or close to typical concentrations in clean ambient air." Is this sufficient for field measurements? It is briefly stated later (p. 5776) in the manuscript that "Some further refinement of the microfluidic technique" will be necessary, but I think a clearer statement is needed in the abstract.

Response: The accuracy and the measurement time of the method are added in the abstract as "*The analytical performance shows good accuracy (6.6 % for GLY and 7.5% for MGLY), suitable precision (< 12.0 %) and method detection limits (MDLs) (80 pptV for GLY and 200 pptV for MGLY) with the time resolution of 30 minutes.* "

Based on its performance in the EUPHORE chamber we believe the method would be appropriate for ambient measurements in a range of field environments which are discussed in Section of "3.3 Method Calibration". In the abstract the following statement has been added "*The microfluidic derivatisation technique would be appropriate for ambient α-dicarbonyl measurements in a range of field environments based on its same performance as other instrument measurements in EUPHORE chamber."*

2. Methods, such as CE-DOAS, BBCEAS, and LIP, have better detection limits and at a much higher time resolution, if I understand the manuscript correctly. In my opinion the lower time resolution has to be discussed in detail. How does this affect

the suitability for field measurements? Is 30 minutes, the measurement time, if I understand correctly, really rapid, as stated on p. 5759? A clarification is needed on the meaning of “rapid”. What is the impact of having a continuous measurement producing, e.g., 1 minute data, and one that provides a 10 minute observation (I was not quite clear on the actual sampling time used for this instrument) every half hour. The method described here benefits from simplicity and cost, but the measurement time aspect could be a disadvantage and I was surprised not to see differences in measurement times clearly addressed.

Response: Unlike the *on-line* techniques of CE-DOAS, BBCEAS, and LIP, the *off-line* microfluidic derivatisation technique includes two separate processes: gas sampling and GC-MS measurement. The sampling time is typically 30 minutes and measurement time is 28 minutes. During the chamber experiment we collected the second sample whilst the first sample was measured on GC-MS. Then the third sample was collected at the same time as the second was measured, and so on. Therefore, a continuous measurement can be realised with each sample of 30 minutes observation. Each data of microfluidic measurement in the figures represents the average concentration of each sampling period and the time of the data point location is the middle time of the sampling period.

The technique is “rapid” by comparison to other off-line derivatisation techniques such as DNPH derivatisation HPLC,PFBHA derivatisation GC-MS or GC-FID methods (but not on-line techniques such as CE-DOAS, BBCEAS and LIP)., the 30 minute sampling time of the microfluidic derivatisation technique is more rapid compared to the 1- 4 hours of DNPH or PFBHA derivatisation offline techniques. DNPH derivatisation with HPLC is the standard method for the detection of atmospheric carbonyl compounds currently employed by the US-EPA (US-EPA, 1999). The use of the word “rapid” has not been put into context in the revised manuscript.

The effect of time resolution on the suitability for field measurements is discussed in the revised manuscript. The time resolution of 30 minutes is more than adequate for *long term* tracking of changes in [GLY] and [MGLY] and for comparison with earth observation and global models. This method would obviously not be appropriate for continuous aircraft measurements.

In the third paragraph of Section 3.3, a detailed description on the detection limit and the time resolution is added as the following.

"The detection limit of this technique on GLY measurement is lower than those of FTIR, SPME, IBBCEAS (Washenfelder et al., 2008), DOAS (Volkamer et al., 2005) and is higher that of BBCEAS, CE-DOAS (Thalman and Volkamer, 2010), Mad-LIP (Huisman et al., 2008), PFBHA mist chamber technique (Spaulding et al., 2002). But the sampling gas volume (250 – 300 L) collected from mist chamber is much higher than that in this study (6 L). For MGLY measurement the microfluidic technique is more sensitive than most spectrometric methods and PTR-ToF-MS (Washenfelder et al., 2008; Thalman and Volkamer, 2010; Volkamer et al., 2005) but less than other PFBHA derivatisation methods (Spaulding et al., 1999 and 2002) due to much lower sampling gas volume. With respect to time resolution, the microfluidic derivatisation technique is lower than all on-line spectrometric techniques since its sampling and measuring processes are separated. The instruments for on-line measurements can complete sampling and measurement simultaneously in a short time varying from 20 seconds to 15 minutes whilst microfluidic technique usually spends ~ 30 minutes to collect sample plus 30 minutes to measure the sample by GC-MS. Although the next sampling process of sample can be conducted simultaneously with the measurement of previous sample, average 30 minutes will be spent on each sample measurement. However, this microfluidic methodology is much simpler and hence has better time resolution when compared with other off-line chemical derivatisation techniques, which need 1-4 hours sampling time and cumbersome and complicated sampling treatments (e.g. Zhou and Mopper, 1990; Spaulding et al., 1999). It should be noted that despite its relatively low time resolution compared with on-line spectrometric instruments, this microfluidic method benefits in its simplicity and cost and is available to most common laboratories with GC-MS or GC-FID. The automation potential, relatively short sampling time and simple sampling treatment compared with other off-line methods are the significant advantages, which are suitable for field measurement and long term observation of GLY and MGLY in ambient air. But the technique is clearly not appropriate for aircraft measurements."

The differences in measurement times among the techniques are listed in Table 2 in this revised paper.

3. In an extension of above: The detection limits of CE-DOAS, BBCEAS and LIP, I believe, are achieved in a shorter sampling time than half an hour. It would be very helpful to clearly state for how long the instrument discussed here samples compared to other instruments. If I understand correctly most of the measurement time is the GC? Also, I was not quite clear on the sampling time of BBCEAS (detection limit is quoted for 10s). For an instrument intercomparison this information is needed.

Response: The sampling times of the FTIR, BBCEAS, PTR-ToF-MS and SPME derivatisation techniques used in this study are 5 minutes, 20 seconds, 5 minutes and 5 minutes, respectively in this study. For FTIR, BBCEAS, and PTR-ToF-MS, the processes of sampling and measurement are conducted simultaneously whilst for SPME derivatisation method the sample is detected using GC-FID after its sampling, as in our methodology. This information is given in Table 2 and described in the section of 2.3.

For comparison purposes, a table (Table 4) is added to show the pairwise correlations among all techniques. The concentration of the continuous measurements is averaged during the same sampling period as the finite grab sample was collected by microfluidic derivatisation technique. The pairwise correlations are estimated by the comparison between the average concentrations of the continuous measurements and those of the finite grab samples collected by microfluidic method.

4. Some of the spectroscopic techniques can have lower detection limits if averaged to longer measurement times, depending on Allan variance analysis etc. The measurement time could be added to table 2 and whether precision and MLD improve with longer measurement time (limited, e.g., by Allan variance analysis).

Response: The measurement time is added to Table 2.

The effect of measurement time on precision and MLD by spectroscopic techniques will be presented in detail in a separate cross-chamber intercomparison paper (for GLY, MGLY as well as NO_2 and aerosol extinction, where appropriate), which is based on more than 20 experiments conducted in the EUPHORE and NCAR chambers using a wide range of spectroscopic

techniques, as well as LIP, PTR-MS and SPME-GC-FID. The performance of each individual technique as well as detailed intercomparison was reported in one conference poster (Thalman et al., 2013).

5. Figure 8 shows two data sets. There are no error bars on the low concentration glyoxal measurements. Is that correct? Is it possible to show a time trace of measurements at constant low glyoxal? That would help convince of the detection limit as no zeroing experiment of the new method is shown. More directly, it would be very helpful to add a lower concentration point, e.g.blank/zeroing to figure 8.

Response: There are error bars on the low concentration of glyoxal. However, the error bars are too small to be display in the figure. The symbols of data point are set to a smaller size to show the error bars in this revised version. It is difficult to show a time trace of measurements at constant low glyoxal since we did not conduct such experiment. A lower concentration point is added in Fig 6b for methylglyoxal but not for glyoxal in Fig 6a.

III) Less important comments:

1. Abstract: line 19-25: “Good and less good”: needs to be more quantitative for an intercomparison paper.

Response: The correlation coefficients are used to quantify the agreements among different measurements as shown in Table 4.

2. p. 5758: Second paragraph. The detection limits, accuracies, precisions and sampling times of these methods need to be mentioned. The mentioned previous PFBHA techniques are being improved upon in this manuscript so a detailed comparison with these is helpful. How does the time resolution of ca. 30 minutes p. 5759 line 12 compare with the previous PFBHA techniques.

Response: The detection limits, accuracies, precisions and sampling times of these methods are now discussed in the revised manuscript. The following is the detailed revision.

“Such as GLY and MGLY were analysed by an on-sorbent PFBHA derivatisation technique with detection limits of 0.1 and 0.6 ppbV and precisions of 2.2 - 5.3 % and 0.7 - 6.4 %, respectively, after 4 hours sampling time (Ho and Yu 2002). MGLY was measured in air by sampling with impingers

filled with an aqueous PFBHA solution with detection limit of 0.02ppbV after 3 hours sampling time (Spaulding et al., 1999) Although derivatisation methods are fully applicable for the measurement of GLY and MGLY, the drawbacks are very long sampling times, with a lengthy and complicated lab procedure of derivatisation and solvent extraction/evaporation following sampling. Sampling times can be reduced to 10 minutes using a Solid Phase Microextraction (SPME) PFBHA on-fibre derivatisation technique (Gomez Alvarez et al., 2009) or a mist chamber with PFBHA solution (Spaulding et al., 2002). However the SPME derivatisation technique suffered from the high detection limits up to 40 ppbV and the mist chamber derivatisation required a large sample gas volume with detection limits of 0.003 and 0.01 ppbV for GLY and MGLY respectively. Furthermore, the preparation processes for PFBHA-coated fibre for SPME are complicated and labour intensive."

3. For the intercomparison: It would be helpful to clearly state how data was selected for the intercomparison. Was data from other instruments binned to the sampling time of the instrument described here (in contrast to measurement time), and how was this achieved, e.g., for SPME or FTIR.

Response: In the first paragraph of section of 3.4, it was described in detail how the data were selected from those samples analysis. The following is the detailed revision.

"In the figure (Fig. 5) for the microfluidic technique each data point shows the average concentration of 30 minutes sampling period for each sample and for BBCEAS each data point indicates the concentration of each 20 seconds. Both FTIR and PTR-MS data points are the concentrations integrated from 5 minutes sampling time. For SPME derivatisation technique each data point implies the average concentration of 5 minutes sampling time every 30 minutes. To intercompare the performances of those techniques and model prediction, the correlations among the various measurement techniques and the modelling calculation in this experiment are estimated and shown in Table 4. The results of continuous measurements such as FTIR, BBCEAS, PTR-ToF-MS and the model were averaged in accordance with the sampling time interval of microfluidic samples. Therefore, the pairwise correlations were estimated based on the results on the same sampling period of all methods."

In Fig. 5, we have not averaged other instrument data to the same time base since we focus here is to compare temporal performance of each technique operating at its typical data rate.

4. p. 5774: The model results require more detail. What was the integration time, how was it initialized, was the direct glyoxal yield from isoprene of Volkamer et al. 2006 and Galloway et al. 2011 included, were any parameters constrained to measurement, e.g., photolysis, isoprene?

Response: More information added with more detail on the model description available in Section 2.7 as "*The box model used in this study also includes a series of 'chamber specific' auxiliary reactions adapted from Bloss et al., 2005 in order to take into account the typical background reactivity of the EUPHORE chamber walls as well as chamber dilution. The model was initiated with measured concentrations of isoprene, NO, NO2 and ozone and constrained to measured HONO, temperature, and relative humidity. The photolysis rate parameterisations used in MCMv3.2 (Saunders et al., 2003) have been adjusted to replicate the photolytic conditions inside the EUPHORE chamber using measured values of j(NO2). More details on the chamber modelling approach used can be found in Rickard et al., 2010*."

The MCM v3.2 mechanism does not currently include the (small) primary GLY yield as discussed by Galloway et al., 2011 but does include a general update of isoprene degradation chemistry, including integration of revised chemistry for isoprene-derived hydroperoxides and nitrates. The major isoprene product, methacrolein, is now represented as a primary VOC and its chemistry is treated in greater detail.

Minor comments:

Line 27 and following: This is based on models. In addition, satellite observations indicate a strong missing source (e.g., Vrekoussis et al. 2009, Myriokefalitakis et al. 2008, Lerot et al. 2010).

Response: We have corrected it. The missing source is described in the sources of glyoxal and the above references are cited.

p. 5755: Line 19 Henry et al. is an odd reference in this context, as the paper was largely instrumental. Citing a modelling study would be much better.

Response: Fu et al., 2008 replaces Henry et al., 2012 as the reference.

p. 5757 Line 1: “specialized” instead of “specialist” I think.

Response: We have changed it.

p. 5757 Line 18 and following. And satellite measurements are usually only available for one time of the day.

Response: This limit of satellite measurements is added in this revision.

p. 5763 Feierabend et al. is using previously developed methods. Please use the ones in prior work.

Response: One previous work by Volkamer, et al., 2005 (J. Photochem. Photobiol., A 2005, 172, 35-46)is cited in this revision.

p. 5773: line 14 “blank sample” It would be helpful to the readers, whether this was chamber air with no carbonyls or zero air from a tank/generator.

Response: The blank sample was collected from the chamber, which had been flushed by outside air for overnight 10 hours. The description is added to explain the blank sample.

Figure 8: I think “FTIR” is mentioned once rather than “microfluidic”in the caption.

Response: It is ‘microfluidic derivatisation’ rather than FTIR in the caption of Fig 8.

Table 2 lists that MDLs are 3 times standard deviation of the S/N of the blank sample chromatograph. However, many methods do not have a chromatograph.

Response: The MDLs are 3 **times standard deviation of the S/N of the blank sample in all instrumental signals not just in chromatograph. We change this definition.**

p. 5754 line 19 and following: Washenfelder et al. 2011 have reported values in Los Angeles that are well below 1 ppb as well and this work should be added to the list of manuscripts. DiGangi et al. 2012 show rural glyoxal and this could also be added as a reference.

Response: The two papers are added as references in this revised paper.

Also p. 5754: Line 19 and following: For which manuscript is the 1820ppt value, or is it the one from Volkamer quoted later?

Response: Yes, it is the quoted paper of Volkamer et al. and we added it into reference.

References

Thalman R., S. Ball, M. Teresa Baeza-Romero, E. Borrás, M. Daniels, I. Goodall, S. Henry, T. Karl, F. Keutsch, S. Kim, J. Mak, P. Monks, A. Muñoz, J. Orlando, S. Peppe, A. Rickard, M. Ródenas, P. Sánchez, R. Seco, L. Su, G. Tyndall, M. Vázquez, E. Waxman, R. Volkamer, Intercomparison of glyoxal and methylglyoxal measurement techniques under simulated atmospheric conditions, International DOAS Workshop August 12-14, 2013 Boulder, CO, USA.

USA EPA, 1999. Compendium method TO-11A.Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [active sampling methodology].

Responses to Referee #2

This paper presents a promising approach for measuring atmospheric glyoxal and methyl glyoxal based on an automated system for generating derivatives ready to be injected into a gas chromatograph. Because the study of atmospheric dicarbonyls remains data limited this is an important contribution. Overall the paper gives a good description of the method and presents the results for specifying the optimal analytical conditions.

I recommend publication pending some minor revision to clarify a few points and give a better sense of the precision. Furthermore, there needs to be a more thorough analysis of the single photolysis run that compared the microfluidic derivitization method to other measurement approaches. What is the meaning of the outlier points where microfluidic derivatisation disagrees with the other methods?

Response: We agree with the reviewer's comments. The outlier of microfluidic method at 240 min compared with other methods has been discussed in this revision, which is ascribed to its longer sampling time (60min) compared with that of other sample (30 min). The longer sampling time may cause a higher enrichment ratio due to more solvent evaporation. The explaination for those outliers especially for GLY after 175 minute may be the memory effect from higher dicarbonyl concentrations at 175 and 240 minute.

——————————— specific comments———————————

page 5758; Its a minor point, but be careful not to oversell this method as being simpler than optical approaches. Whether a technique is simple and straightforward depends on what you are familiar with. To a spectroscopist derivitization and GC-MS will seem incredibly complex, prone to interference and dependent on too many moving parts. You can let this method stand on its merits without having to judge

other methods. Comparing the relative sensitivities and measurement frequency among methods is reasonable, but leave it to the reader to decide what is simple versus complicated.

Response: Firstly, we thank the reviewer for their useful comments. As the reviewer rightly suggests, we have deleted our judgements on other techniques in page 5758. We have clarified that the main advantages of this method are primarily compared to other off-line SPME or denuder type methods and that the technique uses standard off the shelf laboratory instruments/equipment.:

"Although derivatisation methods are fully applicable for the measurement of GLY and MGLY, they need long sampling times, typically 1 – 4 h, with a lengthy and complicated laboratory procedure of derivatisation and solvent extraction/evaporation following sampling of ambient air."

"The detection range of the SPME technique is significantly higher compared with other derivatisation techniques owing to small quantities of derivatisation reagent absorbed on the fibre (Gomez Alvarez et al., 2009). Furthermore, the preparation processes for PFBHA-coated fibre are complicated and labour intensive."

Page 5765 The assertion that a liquid-based calibration approach using pure carbonyl derivatives needs further discussion. Using this as a calibration approach fails to verify that the reaction efficiency is 100% or that the enrichment ratio is constant. Further, it cannot evaluate whether there are any inlet losses. Perhaps this approach can be a component of a calibration scheme, but there also will need to be some evaluation of sampling efficiency and verification of the enrichment and conversion efficiency.

Response: We have evaluated the sampling efficiency. A description on this evaluation and is added to Section 3.3 as "*The reaction efficiencies of derivatisation reaction in micro-reactor were calculated as 92.5 % and 94.3 % for GLY and MGLY, respectively, under the optimal conditions based on the method descripted in our previous study (Pang and Lewis, 2012).*"

We agree there are many other important elements of calibration that are difficult to test. This is the motivation for testing this method against others in

a smog chamber, since all aspects of the system are presented with standard materials. This is the best method available to us for checking potential losses for example on the instrument inlets.

Page 5766 Please say something about the volume of sample collected and the length of time for each sample. Is the air sample time short relative to the 30-minute frequency or does each measurement represents integration over the 30-minute interval? I could not find a specific mention of this detail in the text.

Response: The sample volume is added in the same paragraph and the detailed description is "*A gas sample was collected with a sampling time of 30 minutes at 200 mL/min from the chamber with a sample volume of 6 litres to measure the GLY and MGLY yields from isoprene photo-oxidation using the microfluidic derivatisation technique.*"

The sampling time for each sample is 30 minutes and each measurement data represents integration over the 30 minute interval. This information can be found the end of the first paragraph of the section of 3.4. *"In the figure (Fig. 5) for the microfluidic technique each data point shows the average concentration of 30 minutes sampling period for each sample and for BBCEAS each data point indicates the concentration of each 20 seconds. Both FTIR and PTR-MS data points are the concentrations integrated from 5 minutes sampling time. For SPME derivatisation technique each data point implies the average concentration of 5 minutes sampling time every 30 minutes. To intercompare the performances of those techniques and model prediction, the correlations among the various measurement techniques and the modelling calculation in this experiment are estimated and shown in Table 4. The results of continuous measurements such as FTIR, BBCEAS, PTR-ToF-MS and the model were averaged in accordance with the sampling time interval of microfluidic samples. Therefore, the pairwise correlations were estimated based on the results on the same sampling period of all methods."*

We added the information of sampling time in Table 1 and Table 2.

page 5774 The comparison of microfluidic derivatisation to other methods warrants a fuller discussion. It appears that the other methods and the model simulation all have a similar shape for the evolution of GLY and especially MGLY, but the microfluidic method has a few outliers that show concentrations increasing

when the other methods are already dropping. It would help to present the data in a way that highlighted what is similar and what is different among the methods rather than treating them each separately. Would the figure still be comprehensible to make two larger panels (one each for GLY and MGLY) showing all the measurements simultaneously. With just one experimental run it is hard to know if the outliers are just an analytical glitch, or if the method is responding to some artifact. A comparison to the other methods ought to include some measure of how well they compared that is more quantitative than just stating that they compare reasonably well. Does the new method agree better or worse to the other methods than they do to each other? Perhaps a table showing the pairwise correlations or estimates of bias and offset would be useful here. The problem of comparing continuous measurements to finite grab samples will need to be considered.

Response: We agree with the reviewer's comments. The figure (Fig 5 in current version) is changed into two large panels (one for GLY and the other for MGLY). The outlier of microfluidic method at 240 min compared with other methods has been discussed in this revision, which is ascribed to its longer sampling time (60min) compared with that of other sample (30 min). The longer sampling time may cause a higher enrichment ratio due to more solvent evaporation. The explanation for those outliers especially for GLY after 175 minute may be the memory effect from higher dicarbonyl concentrations at 175 and 240 minute.

A table (Table 4) is added to show the pairwise correlations. The concentration of the continuous measurements is averaged during the same sampling period as the finite grab sample was collected through microfluidic derivatisation technique. The pairwise correlations are estimated by the comparison between the average concentrations of the continuous measurements and those of the finite grab samples.

We appreciate that we only have a small amount of data from a few experiments but consider this a valuable exercise.

page 5776, I think it is overstating things a bit to call the microfluidic method 'rapid' if the sample frequency is only 1/30 minutes. I see that the sample preparation is rapid compared to manual approaches for preparing carbonyl derivatives - the statement here could make a clearer distinction between rapid

sample preparation and rapid sample collection, along with some comment about the need for continuous measurement versus finite sampling or long-duration integrated sampling.

Response: The word of "rapid" is deleted from the conclusion and a clear statement of rapid sample preparation is added. Some comment on the combination of continuous measurement and finite sampling is stated in the conclusion.

The technique is "rapid" by comparison to other off-line derivatisation techniques such as DNPH derivatisation HPLC, PFBHA derivatisation GC-MS or GC-FID methods but *not* on-line techniques such as CE-DOAS, BBCEAS and LIP). The 30 minute sampling time of the microfluidic derivatisation technique is more rapid compared to the 1- 4 hours of DNPH or PFBHA derivatisation offline techniques. DNPH derivatisation with HPLC is the standard method for the detection of atmospheric carbonyl compounds currently employed by the US-EPA (USA EPA, 1999). The use of the word "rapid" has not been put into context in the revised manuscript.

Figure 6 or associated text, the calibration curves need to include uncertainties for the coefficients. The uncertainty will guide choice of how many significant digits to include. I doubt that the coefficients are as precise as implied by presenting them to 6 digits.

Response: The uncertainties of the coefficients and the slopes have been presented in figure and caption.

Figure 8, the uncertainty of the slopes needs to be presented. Is the intercept 'truly indistinguishable from zero?#

Response: The uncertainties of the coefficients and the slopes have been presented on figure. No, but the intercept is truly close to zero. In this revised manuscript, the linear line is not forced to pass through zero.

Reference

USA EPA, 1999. Compendium method TO-11A.Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [active sampling methodology].