Response to Interactive comment on "Evidence for an unidentified ground-level source of formaldehyde in the Po Valley with potential implications for ozone production" by J. Kaiser et al.

Anonymous Referee #1

We thank the referee for the valuable comments. The original comments are shown in italicized black, while responses are provided below in blue.

In this paper Kaiser et al have measured HCHO from the Zeppelin NT platform over the Po valley in Italy. The measurements are made using a highly sensitive in situ instrument based on LIF spectroscopy, and with good time resolution. The combination of this instrument and the Zeppelin platform enable some unique measurements to be made of HCHO in the first 1 km of the boundary layer. The main result from this paper is that the measurement cannot be reconciled with the results from a 1D model of the atmosphere without invoking a surface source emission of HCHO, and from an analysis of the vertical profile of HCHO, and the origin of the airmass, the authors, after ruling out several possibilities, conclude that agricultural emissions of HCHO from the surrounding countryside are responsible for the gap between measurements and models. There is good supporting suite of measurements on the Zeppelin which are used to help formulate this conclusion. Most of the discussion of the other measurements are in separate papers. There are some assumptions which have been used to make this conclusion, and which are discussed in the paper. The results are important as the Po valley is a notoriously polluted location, with ozone, whic is formed as a result of further degradation of HCHO, being often above the EU exceedance limit value.

The results are not totally new, there was a previous study in this region in the FORMAT campaign, where HCHO was underestimated by a model, but the identification of the missing HCHO from local agricultural sources is new. Also in this study measurements of OH reactivity are available, which enable confidence to be gained that all the OH sinks are inputted into the model (i.e. that it is not a problem with missing OH sinks in the model which leads to an underestimate of the HCHO levels). An impact of the work is that additional ozone is generated from the missing HCHO. The paper is suitable for publication in ACP. But I would like to authors to consider the points below prior to publication in ACP.

Specific points

Page 25145. Line 2. Why is the precision varying over such a wide range (20-200 pptv?). Although it is related to the precision and the sensitivity of the instrument, it would be useful to state the range of limits of detection exhibited by the instrument during the campaign.

Precision derived from measurements of synthetic air is $\sim$ 20 ppt in 1 s. For higher concentrations, precision is derived from the standard deviation of the measurement at a constant

concentration (~200 ppt at 3 ppb). Our empirical determination of precision does not deviate from what would be anticipated for a shot-noise limited detection scheme. The limit of detection is calculated from the precision of the measurements of synthetic air, and is now stated in the manuscript (2σ LOD = 40 ppt).

Page 25145. Line 18. MCM v3.2 is the most to date version of the MCM, but this update was given quite recently, and so Saunders et al., 2003 seems too old a reference to the MCM. Is there a more up to date reference which describes some of the changes in the MCM with version 3.2?

The reference has been changed to reflect the citation suggested on the MCM website. This includes the website url, so that the reader can reference the version used in this manuscript and any future alterations.

Some further justification of the NH background value of CH4 used in the model is needed, even if it is to say there are no emissions of CH4 anywhere close (e.g. from natural gas lines, extraction activity from fracking etc.).

As noted by the second referee, emissions from agriculture (rice paddies and livestock) and natural gas fields may lead to enhanced CH_4 in the Po Valley.

We have recently received measurements of CH_4 in the Po-Valley from a mobile aerosol and trace gas laboratory ("Measurements Of Spatial QUantitative Immissions of Trace gases and Aerosols": MOSQUITA; Bukowiecki et al., 2002; Mohr et al., 2011), which was equipped with a Picarro Cavity Ring-Down Spectroscopy instrument. MOSQUITA-based CH_4 measurements were acquired from 8 June 2012 to 9 July 2012 (Figure R1). While measurements are not available on the day used in these model simulations, the average measurement acquired in the flight region of the Zeppelin is likely applicable to this study. The average mixing ratio of 2355 ppb is higher than the global average of 1760 ppb initially used in the model.

Though the increased methane concentration has little impact on our analysis and no impact on our conclusions, all model runs presented in the manuscript now use the average MOSQUITA CH_4 measurement.

Line 8. Please state the % total of the OH reactivity which is from NOx and CO, as this will provide a useful guide as the importance of the VOCs towards OH reactivity in this environment. Also, what % of the OH reactivity comes from HCHO itself? The MS only states that HCHO is the largest contributor from the VOCs.

The relative contributions of NO_X (41%), CO (13%), and all measured VOCs and OVOCs (26%, including HCHO which is 8%) to modeled OH reactivity in the boundary layer (100 m) at 8:45 AM are now included in the manuscript.

Page 25148. Line 24. "compared" and not "compare"

Corrected.

Page 25149. Given that this paper discusses quite a bit the sinks for OH via the OH reactivity measurements, and that HCHO levels are related to the concentration of HO2, I was surprised not to see a discussion about the significant missing gas-phase source of HONO from HO2 inferred from the Zeppelin measurements and reported earlier this year. Are these findings not relevant to this study in any way? I realise that most of this current paper is about the mixed layer close to the surface, whereas the Science paper was about missing HONO sources from HO2 in the residual layer which was disconnected to the BL early in the morning, but some links to the other paper might be made?

Because the proposed mechanism forming HONO presented by Li et al. (2014) has not been confirmed, no additional gas-phase HONO formation mechanism is included in our model. While the source of HONO is uncertain, it is unlikely to affect analysis of the HCHO budget as HONO, OH, HO_2, and NO_X are constrained to measurements.

Page 25152. Line 20. Why did measured HO2 have a large uncertainty? This has the led the authors here not to compare HO2 levels to a model, which is a shame, as a lot would have been learnt from this. In the Science paper earlier this year HOx levels were compared to the model. Did the HO2 measurements just have a larger uncertainty for this portion of the study?

Page 25152. Line 16. HCHO is responsible for about 45% of the HO2 production, it is a shame that the measured HO2 values could not be used, as there is clearly a critical link between HO2 and HCHO. What was the uncertainty of the HO2 measurements? Some discussion is needed otherwise the statement that the model runs produced HO2 within the uncertainty of the measurements is not helpful. Not including all HCHO sources has significant effects on the modelled HO2 concentrations (line 17), and so a discussion of measured/modelled HO2 provides confidence in this earlier statement. Given that HO2 dominates the production of O3 (line 16) not being able to use the measured HO2 is a weakness of the approach. Also consistency between measured HO2 and HCHO would help to confirm that there are missing sources of HCHO in the model.

As described in the supplement of the Li et al. (2014), an NO related interference causes the HO_2 measurement to be positively offset. In the laboratory, the offset was measured to be (0.7 ± 0.2) x 10^8 molecules/cm^3. In the field, the measured value varied between 1.7 x 10^8 and 3.9 x 10^8 molecules/cm^3. The reported data is corrected using lab-based measurements, which may misrepresent the actual offset by as much as 3 x 10^8 molecules/cm^3. The cause for the discrepancies in the measured offsets is unclear.

The reported accuracy for the HO_2 measurements (24-30%, 1σ) is based on the error and reproducibility of calibrations. Boundary layer measurements are as low as 1 x 10^8 molecules/cm^3. Because the measurements are near the value of the offset, and because the uncertainty in the offset is as much as 3 times the measurement, there is limited value in

comparing measured and modeled HO_2. The difference in concentration of HO_2 between the two model scenarios is ~12%, which is smaller than the measurement uncertainty calculated from calibrations and nearly invisible when viewed alongside the uncertainty associated with the offset (Figure R2).

Because the HO_2 measurements cannot provide further quantitative insight into this analysis, we rely on the two modeled HO_2 scenarios discussed in the text. Alternatively, the reported HO_2 and modeled HO_2 (using modeled HCHO) could be used to calculate missing O_3 production. This leads to a much larger missing $P(O_3)$, as the discrepancy in HO_2 concentrations between the two scenarios is then ~60%. Given the uncertainty in the HO_2 measurements, using two model scenarios is a more conservative and realistic depiction of the effect of HCHO sources on $P(O_3)$.

The same flight data is used here as in Li et al. (2014). In that analysis, "observed" HO_2 + HO_2H_2O is higher than the modeled scenario, and this is attributed to an offset in HO_2 measurements (see caption of Figure 4). However, because the authors use modeled HO_2 + HO_2H_2O rather than the observations in their analysis, this does not influence their conclusions. Similarly, we use model HO_2 so that conclusions are not influenced by potential measurement issues.

Page 25159. It would be useful in the Table to make an explicit statement of the LODs which are related to the precision. For the Spectroradiometer entry in the table, it was not clear what the "-" means?

Both the accuracy and precision of the measured J values are dependent on conditions and the photolysis process. Two examples of photolysis frequencies as examples are:

$j(NO_2)$: LOD approx. 1×10^{-7}/s, accuracy approx. 5%

$j(O^1D)$: LOD approx. 5×10^{-8}/s, accuracy approx. 10%

LODs are derived from nighttime measurements of a Zeppelin radiometer before and after the 2012 campaign. The 15% accuracy is a conservative "mean" for all photolysis frequencies because for some species photolysis quantum yields are poorly known.

The HCHO LOD is now explicitly stated in the manuscript.

The OH and HO_2 precisions currently listed in the table are given as the limit of detection.

For VOCs, precision and LOD is substance dependent. Substance-specific LODs are provided in the cited reference.

This leaves k_{OH}, HONO, NO_x, O_3, and CO. For these parameters, the LOD can be calculated from the precision reported in the table. This information is now clarified either by footnotes, available in the cited references, or stated within the text of the manuscript.

Page 25162. Figure 3. Base model and the other legend labels need some supporting statement in the caption, even if to refer to some text in the main body of the MS.

The caption has been altered to refer readers to the text for detailed model scenarios descriptions.

Page 25163. Figure 4. A plot of OH reactivity with altitude would be instructive here, as it is difficult to see the direct link between OH reactivity and altitude here. Also why are only data during the ascents included in the figure, this wasn't clear.

A plot of OH reactivity with altitude is given in Fig. 2 and Fig. 3.

Descents were performed ~3 times more quickly than ascents. Instruments with lower time resolution (i.e. VOCs) acquired only a few measurements during the descent, with each measurement representing a large vertical range. Because vertical spatial resolution is important to our analysis, we restrict ourselves to the data acquired during the ascents. This is now clarified in the manuscript.

 Page 25164. Figure 5. I think the equations of the lines are not necessary on the figure. They detract from the clarity of the figure and the values do not make immediate sense in the context of the figure. There are no data after 1100 on the figure, so I didn't understand how a line could be fitted to data after 1100 ("top"). Add the word "line" to bottom, middle and top? This figure and the explanation is not that clear.

The figure has been altered to only show mixed layer measurements, and linear fits are removed. The caption now states the main point: There is little variation in mixed layer CO, and the correlation with HCHO is small (r^2=0.29).

Page 25165. Figure 6. Be clear in the caption that it is the difference in modelled O3 for HCHO (calculated) minus modelled O3 for HCHO (measured) (and not the other way around).

The caption has been reworded. Missing $P(O_3)$ is defined as $P(O_3)$ calculated using measured HCHO minus $P(O_3)$ calculated using modeled HCHO.

References

Bukowiecki, N., Dommen, J., Prévôt, A. S. H., Richter, R., Weingartner, E., and Baltensperger, U.: A mobile pollutant measurement laboratory – measuring gas phase and aerosol ambient concentrations with high spatial and temporal resolution, Atmos. Environ., 36, 5569–5579, doi: 10.1016/S1352-2310(02)00694-5, 2002.

Mohr, C., Richter, R., DeCarlo, P. F., Prévôt, A. S. H., and Baltensperger, U.: Spatial variation of chemical composition and sources of submicron aerosol in Zurich during wintertime using mobile aerosol mass spectrometer data, Atmos. Chem. Phys., 11, 7465-7482, doi:10.5194/acp-11-7465-2011, 2011.
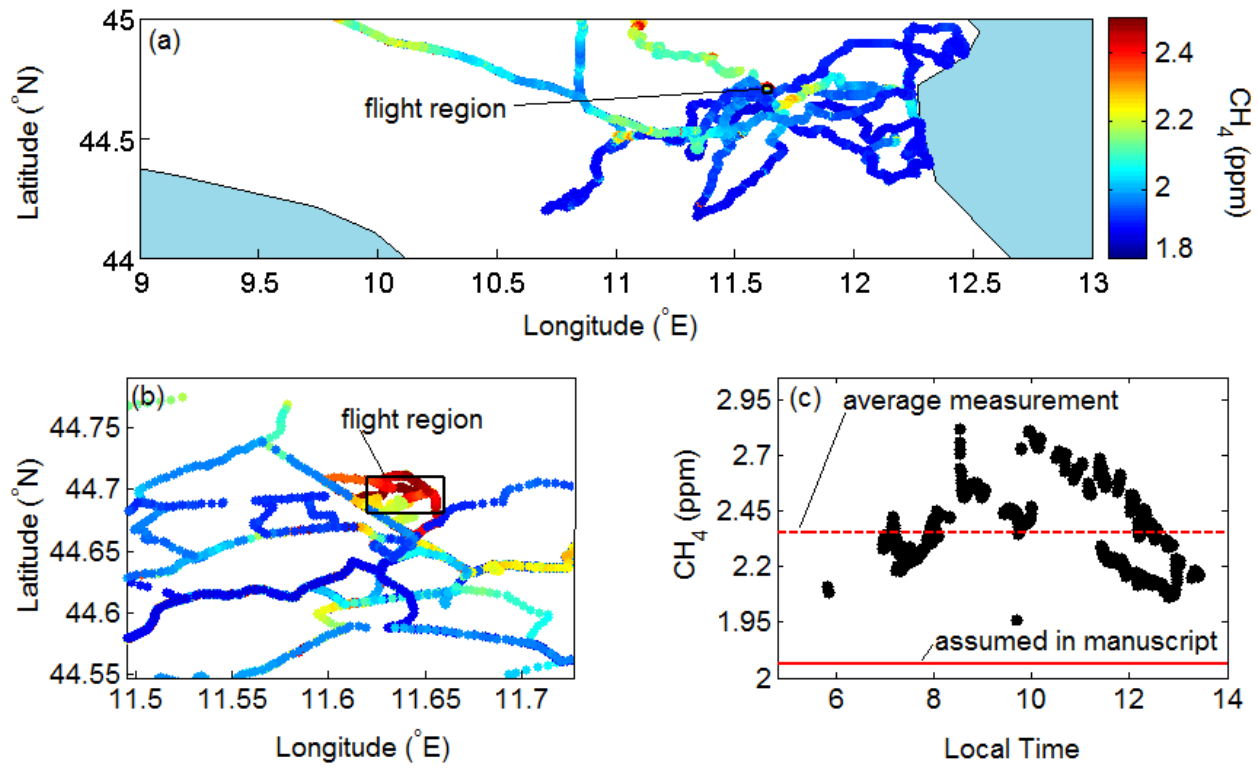
Figure R1. (a) Po-Valley methane measurements acquired from the MOSQUITA during PEGASOS 2012. (b) Zoomed in region highlighting the enhanced methane in the flight region. (c) Time series of methane measurements acquired in the boxed region of (b).
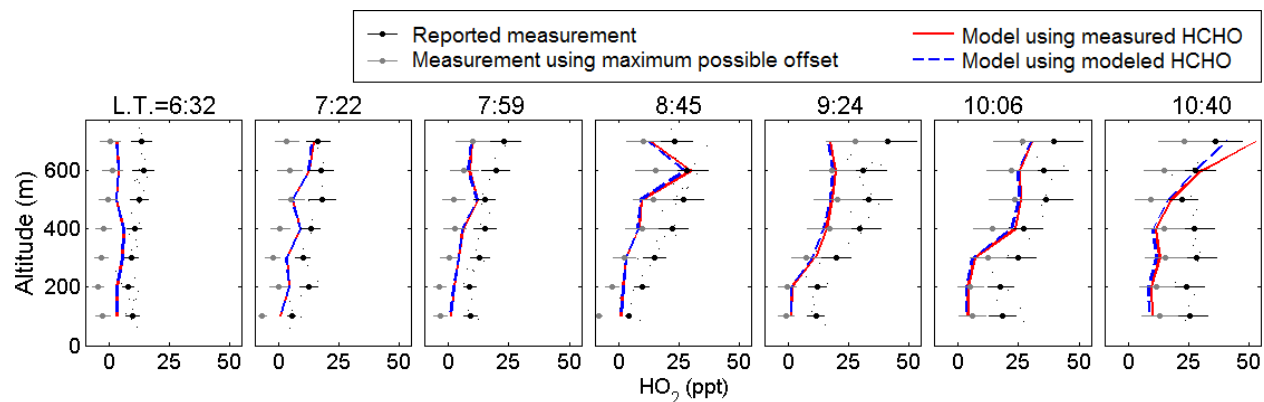
Figure R2. Reported HO$_2$ and the lower limit on HO$_2$ measurements based on the uncertainty in the measurement offset. Error bars represent a 30% 1σ uncertainty. Modeled HO$_2$ concentrations refer to the two scenarios in the manuscript used to investigate missing P(O$_3$).