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## ***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**

Received and published: 27 November 2014

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

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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, which 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.

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?

Some further justification of the NH background value of CH<sub>4</sub> used in the model is needed, even if it is to say there are no emissions of CH<sub>4</sub> anywhere close (e.g. from

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natural gas lines, extraction activity from fracking etc.).

25148. Line 8. Please state the % total of the OH reactivity which is from NO<sub>x</sub> 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.

Page 25148. Line 24. “compared” and not “compare”

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 HO<sub>2</sub>, I was surprised not to see a discussion about the significant missing gas-phase source of HONO from HO<sub>2</sub> 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 HO<sub>2</sub> in the residual layer which was disconnected to the BL early in the morning, but some links to the other paper might be made?

Page 25152. Line 20. Why did measured HO<sub>2</sub> have a large uncertainty? This has led the authors here not to compare HO<sub>2</sub> levels to a model, which is a shame, as a lot would have been learnt from this. In the Science paper earlier this year HO<sub>x</sub> levels were compared to the model. Did the HO<sub>2</sub> measurements just have a larger uncertainty for this portion of the study?

Page 25152. Line 16. HCHO is responsible for about 45% of the HO<sub>2</sub> production, it is a shame that the measured HO<sub>2</sub> values could not be used, as there is clearly a critical link between HO<sub>2</sub> and HCHO. What was the uncertainty of the HO<sub>2</sub> measurements? Some discussion is needed otherwise the statement that the model runs produced HO<sub>2</sub> within the uncertainty of the measurements is not helpful. Not including all HCHO sources has significant effects on the modelled HO<sub>2</sub> concentrations (line 17), and so a discussion of measured/modelled HO<sub>2</sub> provides confidence in this earlier statement.

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Given that HO<sub>2</sub> dominates the production of O<sub>3</sub> (line 16) not being able to use the measured HO<sub>2</sub> is a weakness of the approach. Also consistency between measured HO<sub>2</sub> and HCHO would help to confirm that there are missing sources of HCHO in the model.

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?

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.

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.

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.

Page 25165. Figure 6. Be clear in the caption that it is the difference in modelled O<sub>3</sub> for HCHO (calculated) minus modelled O<sub>3</sub> for HCHO (measured) (and not the other way around).

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