# 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 #2**

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

*General remarks:*

*The manuscript describes detailed measurements of atmospheric trace gases taken within the planetary boundary layer from a Zeppelin airborne platform compared to a modeling study of air chemistry in the early morning hours. The measurements cover a wide range of chemical components compiled to constrain a direct comparison between model and experiment to identify possible gaps in our knowledge of sources and sinks of air chemistry or pollution relevant compounds. The paper is well structured and written in a concise way. It is made clear, that the model and experiment differ significantly in the concentrations of formaldehyde. However, the statement that the most probable source of missing HCHO is the direct emission from the soil and plant matter below the Zeppelin is not confirmed by the data given.*

While we agree that we do not have unequivocal proof of direct emissions from soil and plant matter, our data does provide evidence of an unidentified ground-level source of formaldehyde, as stated in the manuscript title. Because measured and modeled OH reactivity are in good agreement, this additional source cannot be photochemical in nature. As direct emissions from anthropogenic sources are ruled out, and because agricultural activity in the surrounding area was high, soil and plant matter more likely than any other source of direct HCHO emission. Specific concerns are addressed below.

*Specific comments:*

*Model simulations:*

*The model is using a global background concentration of methane, a precursor of formaldehyde (not measured from the Zeppelin, nor on the ground) of 1760 ppb. That is probably not realistic in the Po-Valley where major methane emissions are from agriculture (rice paddies and livestock). With the diurnal variation of the planetary boundary layer nighttime methane concentrations in agricultural areas could be far higher. (see for example www.gl.ethz.ch/news/Bamberger_etal.pdf). Such a variability of the methane, which is one of the precursors of formaldehyde in the Po valley, is not discussed but could affect also the early morning chemistry. Methane also provides a large fraction of the OH reactivity especially in the lowest layers (Fig.4). There are also other sources for methane in the vicinity of the SPC station*

*which could contribute to the diurnal variability and nighttime enhancements below the nocturnal inversion. Within the Po-valley there are at least 50 natural gas fields, several very close to SPC. It should be discussed how such variable methane concentrations affect the model results.*

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.

We have repeated the base-case scenario using the average of the MOSQUITA measurements. Results are shown in Figure R2. The effect of $CH_4$ on modeled OH reactivity and HCHO is negligible. The model scenario using high concentrations of ethene show that modeled and measured HCHO and OH reactivity cannot be brought into agreement by adding any photochemical HCHO precursor. Because ethene has a higher yield of HCHO per OH reactivity, the model scenario currently presented in the manuscript addresses the concern of photochemical HCHO production more fully than a model scenario with increased $CH_4$.

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.

*Model sensitivity to turbulent mixing (supplement): This discussion shows the variable eddy diffusion is not changing the results. This discussion could be shortened in case, the model can be constrained to the measured 3D wind –measurements (page 25145, line 12).*

The SCM has actually been constrained with 3D wind fields but not those measured by the Zeppelin. The reason not to use the Zeppelin 3-D wind field observations is that they only cover a limited timeframe of the simulations covering multiple days. Alternatively, for studies with the SCM in support of analysis of observations such as those collected in the PEGASOS campaign we generally use the ECMWF re-analysis data to consider the role of advection and changes in synoptic conditions. This generally results in a quite realistic simulation of the actual meteorological conditions encountered during the campaign. However, we wanted to assess the sensitivity of the simulated reactive compound concentrations to turbulent transport being key to boundary layer exchange of tracers with lifetimes such as HCHO and its precursors. We feel the supplemental information provides useful information justifying the assumptions made in the manuscript (particularly, that the vertical mixing is accurately represented in the model

framework, and that reflective boundary conditions are appropriate). Because the discussion is in the supplement, it does not distract from the text.

*Potential sources of HCHO: page 25149 line 16 to 29. A source region of Bologna (southwest of SPC) could be more simply excluded using a HYSPLIT backtrajectory, and on line wind measurements onboard the Zeppelin. A backtrajectory analysis could also help to investigate whether other sources of HCHO (or CH4?, or biofuel) could possibly be located upwind of SPC.*

As discussed above, we can exclude photochemical sources of HCHO such as biofuel and methane. This leaves the possibility that HCHO is transported from a source region with high HCHO. The main wind direction was from W to WNW; wind speeds were generally low between 0 and 6 m/s (Fig. R3). The manuscript does not state that transport from Bologna is impossible, but that only 90 ppt (7% of the missing HCHO) can be accounted for if the air is transported from Bologna.

To determine if Bologna or other source regions can be excluded as potential HCHO sources, an ensemble of 4-hour and 12-hour kinematic back trajectories (BTs) were calculated using the HYbrid Single-Particle Lagrangian Integrates Trajectory (HYSPLIT) model (Draxler and Rolph, 2003), initializing at each hour, and ending at the approximate time and location of the observed rise in HCHO (44.695°N, 11.64°E, 300 m asl, 7 UTC). The Global Data Assimilation System archive was used for meteorological inputs.

Because there is large variability in the calculated back trajectories, HYSPLIT analysis neither excludes nor highlights potential sources of advected HCHO, including Bologna (Figure R4 and R5). For this reason, and because the analysis currently presented in the manuscript places an upward bound on the potential role of advection, we do not feel it would benefit the manuscript to include HYSPLIT outputs.

*Implications for ozone production: Are there any ground based ozone measurements available at SPC that could be use to confirm the model? How do they agree with ozone measurements from the Zeppelin?*

In the calculations for ozone production rates, ozone mixing ratios are constrained to the measured values. Calculations of ozone mixing ratios or $O_3$ vertical structure depend on chemical and physical processes that are beyond the scope of this paper.

*printing errors in the supplement page 3, line 17, remove ..as..*

Corrected.

*page 4, line 6: significantly*

Corrected.

**Acknowledgements**

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this publication.

**References**

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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.

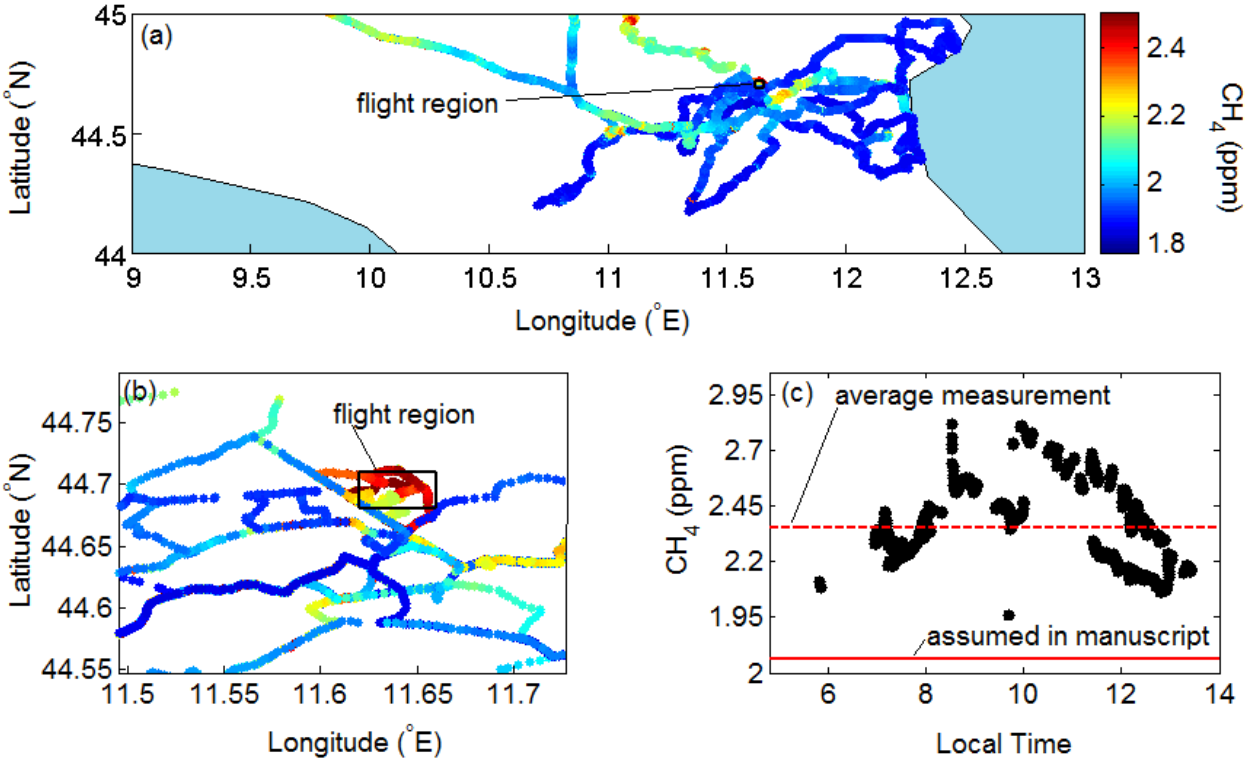


Figure R1. (a) Po-Valley methane measurements acquired from the MOSQUITA during PEGASOS 2012 (b) Zoomed in region highlighting the enhanced methane in the flight region (c) Time series of methane measurements acquired in the boxed region of (b).

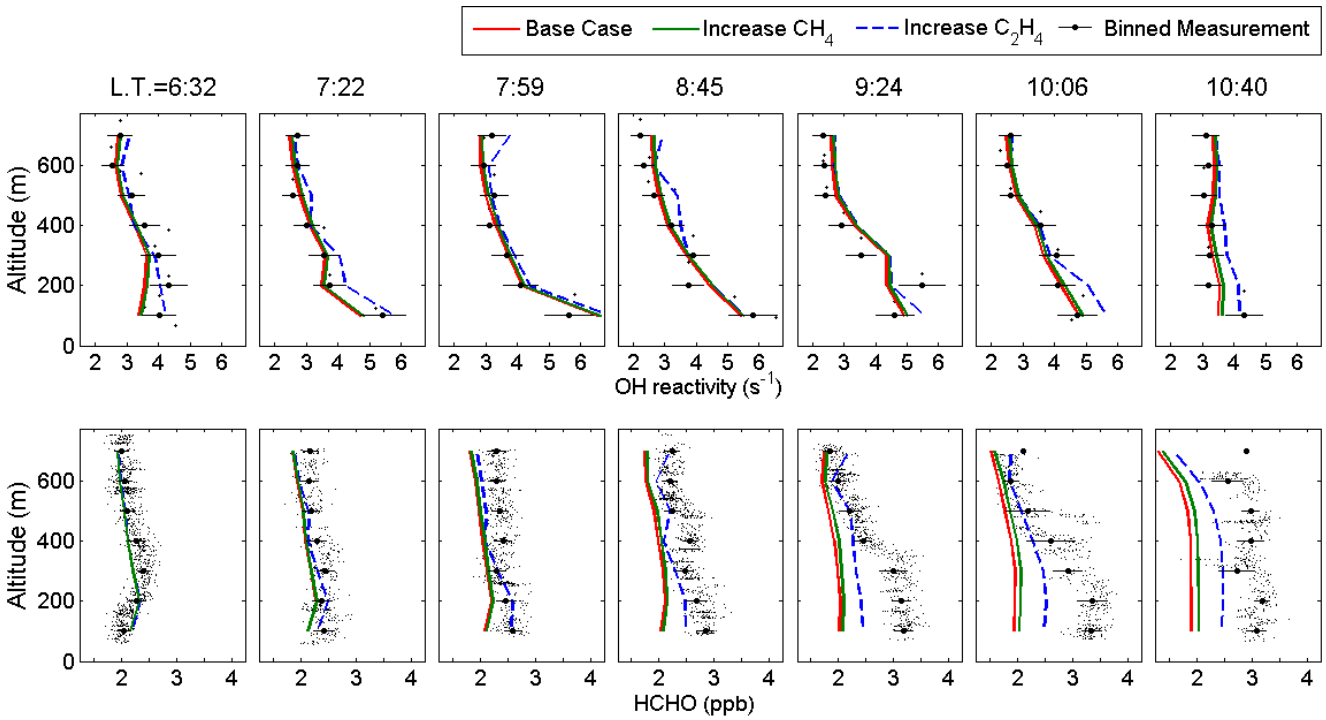


Figure R2. Modeled and measured HCHO and OH reactivity for the base case and increased ethene scenarios as described in the manuscript and shown in Figure 3. The increased $CH_4$ scenario represents the base case scenario altered such that the average of the MOSQUITA measurements (2355 ppb) is used rather than the global background (1760 ppb).

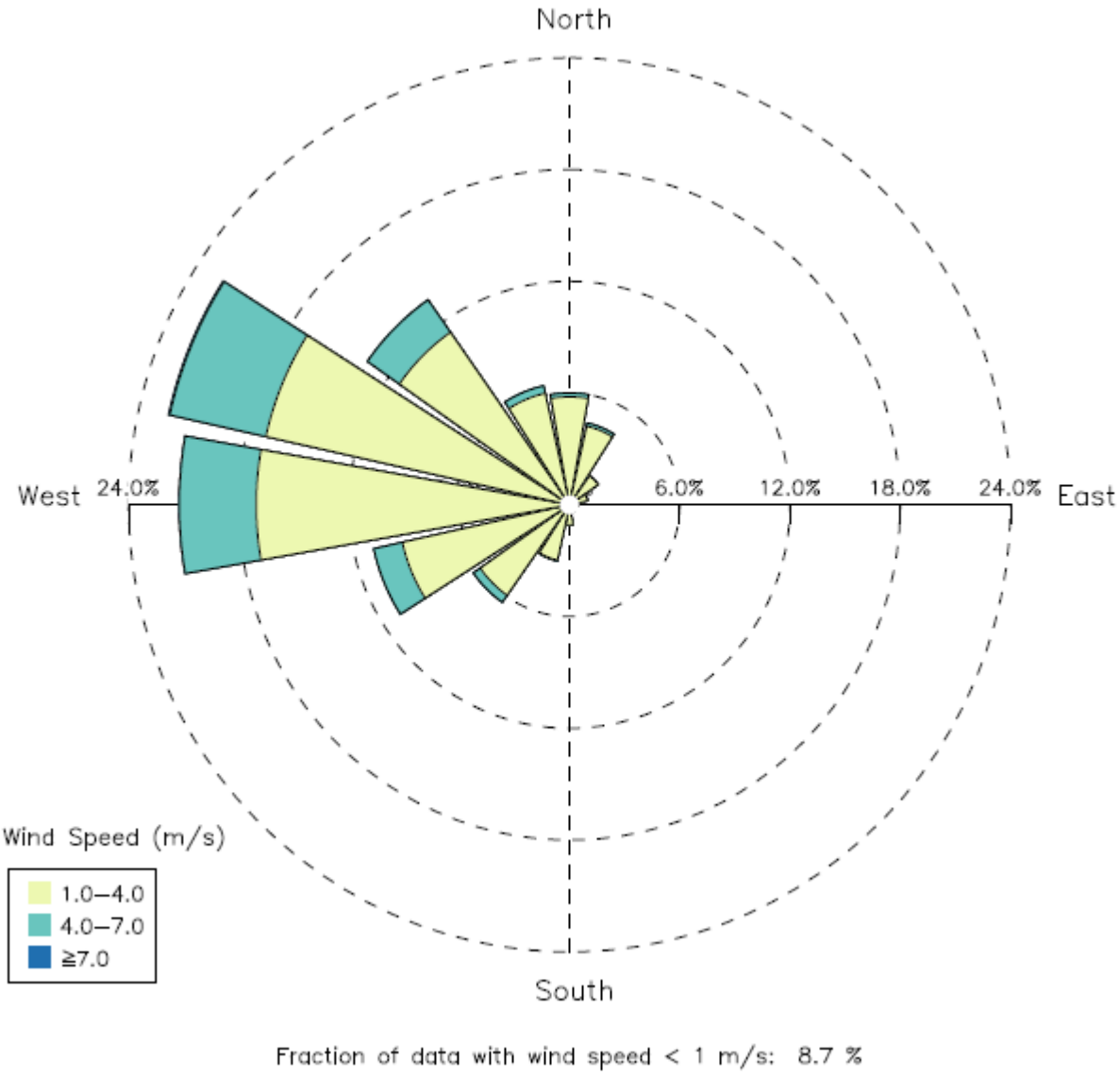


Figure R3. Wind measurements acquired on the July 12th flight.

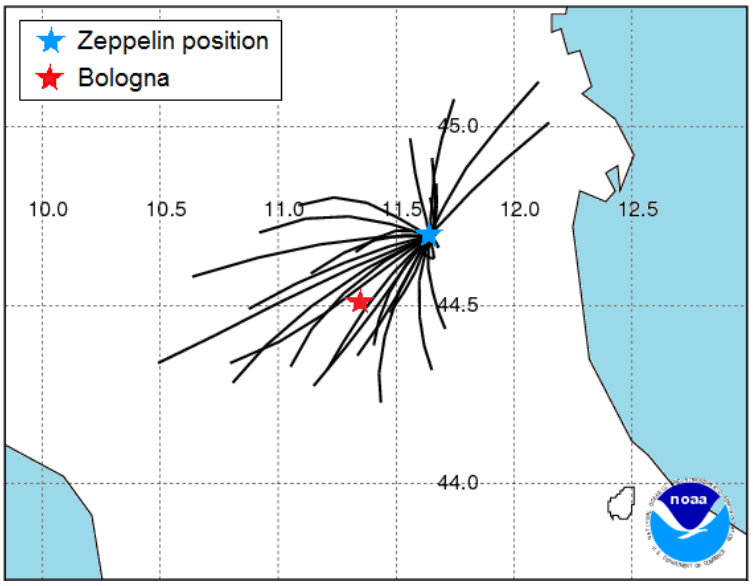


Figure R4. 4 hour HYSPLIT backtrajectories ending at the Zeppelin's position at the time of the observed increase in HCHO.

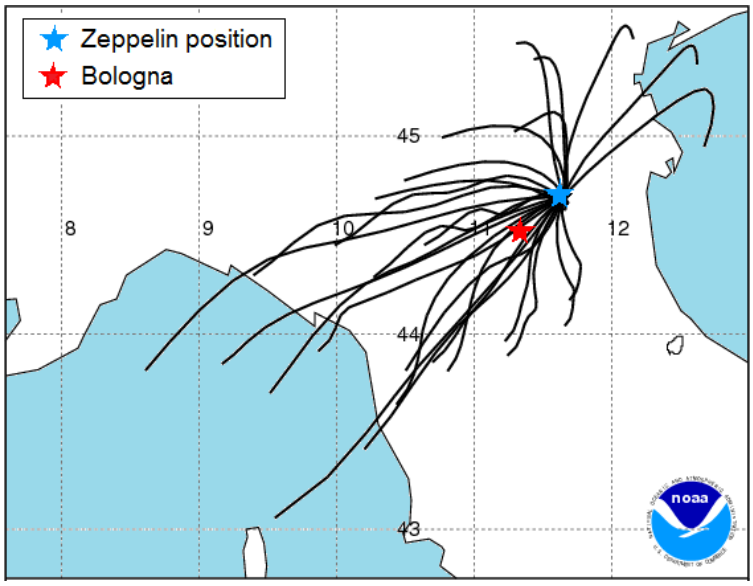


Figure R5. 12 hr HYSPLIT backtrajectories ending at the Zeppelin's position at the time of the observed increase in HCHO.