

We would like to thank the referees for their comments on the manuscript and give detailed responses where appropriate.

Referee 1

All minor typographical errors have been corrected.

1. We have now included typical ion counts and the E/N values. The following sentence has been included

Typical reagent ion values were $\Gamma = 1.5 \times 10^6$ Hz, and $I_{\text{H}_2\text{O}} = 2.5 \times 10^6$ Hz. The pressure in the CDC was 0.25 Torr, where the local electric field divided by the gas number density (E/N) was 180 Townsend ($\text{Td} = 10^{-17} \text{ V cm}^{-2}$).

2. The details of the reagent ion gas mixture have now been included and the following sentence added

The mix was produced using a manifold by evaporating the liquid deionised H₂O and CH₃I sequentially into the manifold to reach the following partial pressures of 10 Torr H₂O and 15 Torr CH₃I, before adding 5 bar of N₂ to make a ionization gas mixture of 0.39 % CH₃I and 0.26 % H₂O. Methyl iodide CH₃I (≥ 99.5 %) was purchased from Sigma Aldrich and used as provided.

3. This is a synthetic standard. The text has been altered to read

The dilution factor was determined by the dilution of the toluene, referenced to a certified synthetic standard (Apel Reimer, USA) as outlined by Yates et al, (2010).

4. The text has been moved to the discussion section as suggested.

6. The figure errors have been corrected and the data in Figure 2 is from another flight (as mentioned in the figure legend), hence the difference in concentrations.

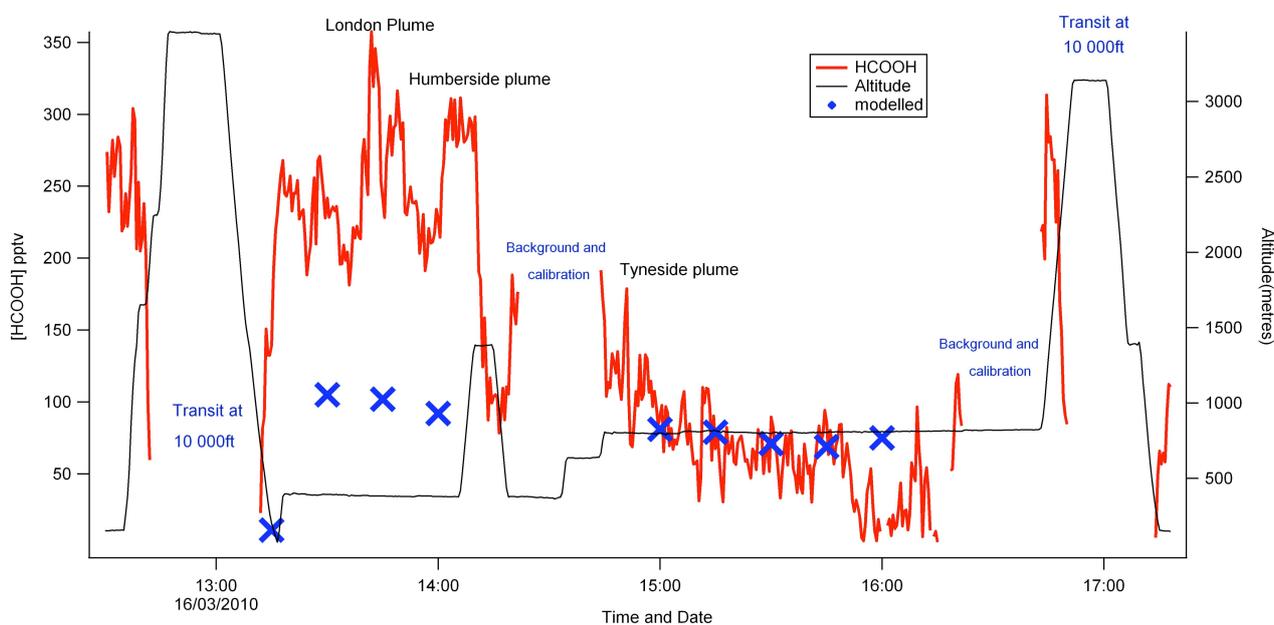
Referee 2.

1. Carboxylic acids with OH

The rate coefficients for saturated carboxylic acids are slow, however there has only been one study of the reaction of OH with an unsaturated organic acid (Tereul et al., 2007) and the referee is correct that the rate constant is quite large ($2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The rate coefficients for

Methacrylic and crotonic acid were estimated rather than measured (Calvert et al., 2011). The manuscript has now been altered to include the term “saturated acids”.

2. The referee also asks for the trajectory modelling section to be improved. More data has been included in Figure 8, as shown below



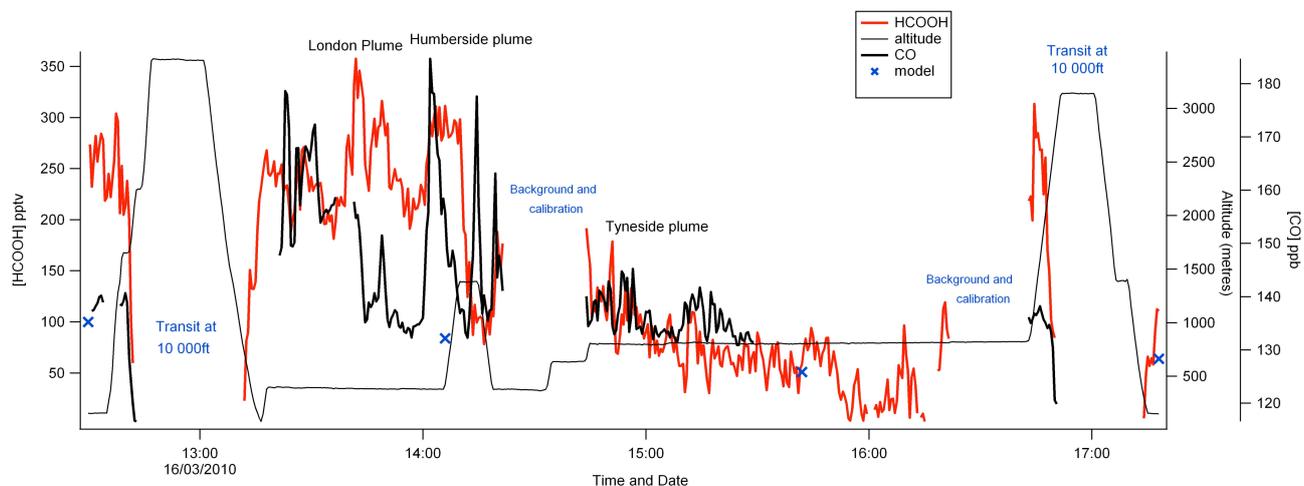
The conclusions are still the same, i.e. the model under predicts HCOOH formation in the atmosphere. Other field studies have also encountered difficulties in ascribing sources to the high concentrations of carboxylic acids that are observed, particularly in periods outside the growing season when biogenic emissions of isoprene are considered to be minimal (*e.g.* Talbot et al., 1988, 1995; Rinsland, 2004). Such discrepancies between perceived source strengths and observed atmospheric concentrations have led many authors to speculate upon the existence of a missing or poorly constrained source term (*e.g.* Grosjean, 1989; Talbot et al., 1988, 1995; Granby et al., 1997; Rinsland, 2004), and it has been suggested by several of these studies that an unknown anthropogenic, and perhaps secondary source may be responsible. Indeed work by the authors, have suggested that there is a direct source of HCOOH from combustion (Archibald et al., 2008) Within the manuscript we state that the discrepancy is due to anthropogenic sources, it may be direct emissions, it may be fast reacting alkenes from anthropogenic sources that we don't model. However, we don't think it is biogenic emissions because they are too low at this time of year based on urban and rural measurements from archive UK air quality data. So we are not ruling out secondary sources we are merely stating that it is unlikely to be biogenic in this instance.

3. CO

There will be some relationship between CO and HCOOH because they are both derived from anthropogenic sources (which we believe to be the case here). However, ozonolysis of 1-enes, necessary to produce CH₂OO and hence HCOOH will produce predominantly ketones as the co-product



where R₁ and R₂ are both alkyl groups. Ketones are known to be slow reacting and hence there is no direct connection here between CO and HCOOH production. Of course, where polluted plumes occur one will see elevated CO and if HCOOH is produced from primary emissions and as an oxidation product then we will see elevated levels too. These data presented, do show elevated CO and HCOOH during the plume events but they do not overlay one another and there is no reason that they should. The figure below also includes the CO data from the flight, it clear that CO captures plumes in the same area. However, as explained it is not expected for there to be a direct correlation with CO as a result of the different sources.



4. Flow regimes

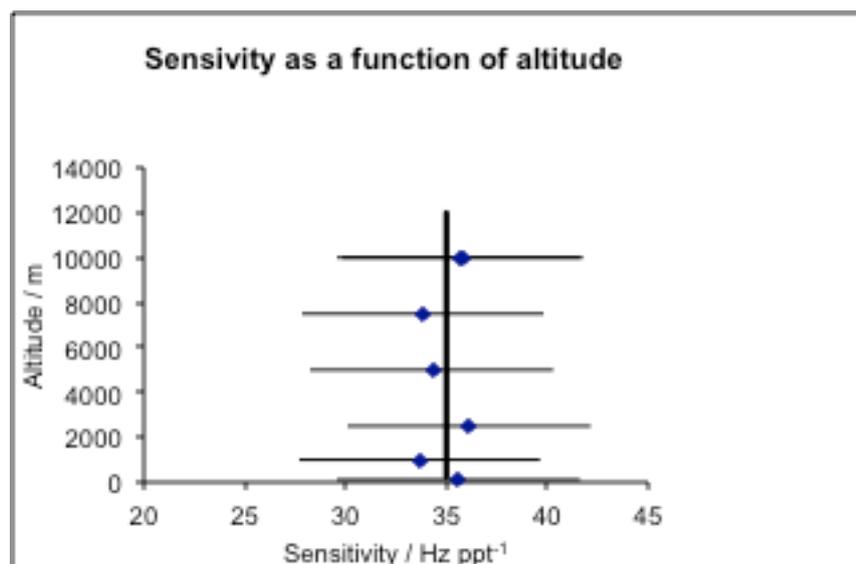
The following has been added to the manuscript to include how flows were controlled and measured.

Sample flow through the orifice was 0.8 SLM on the ground. The pressure in the ionisation region was set and controlled to 22 Torr and thus the flow through the orifice changes slightly with ambient pressure. Flows were controlled and measured using a mass flow controller (MKS 1179

and MKS M100 Mass flow controllers, MKS Instruments, UK) and Baratron (1000 Torr range, Pressure Transducer, Model No. 722A, MKS Instruments, UK).

5. Sensitivity as a function of altitude

The figure below shows the sensitivity as a function of altitude, the standard deviations in the calibration factor have been included in the manuscript.



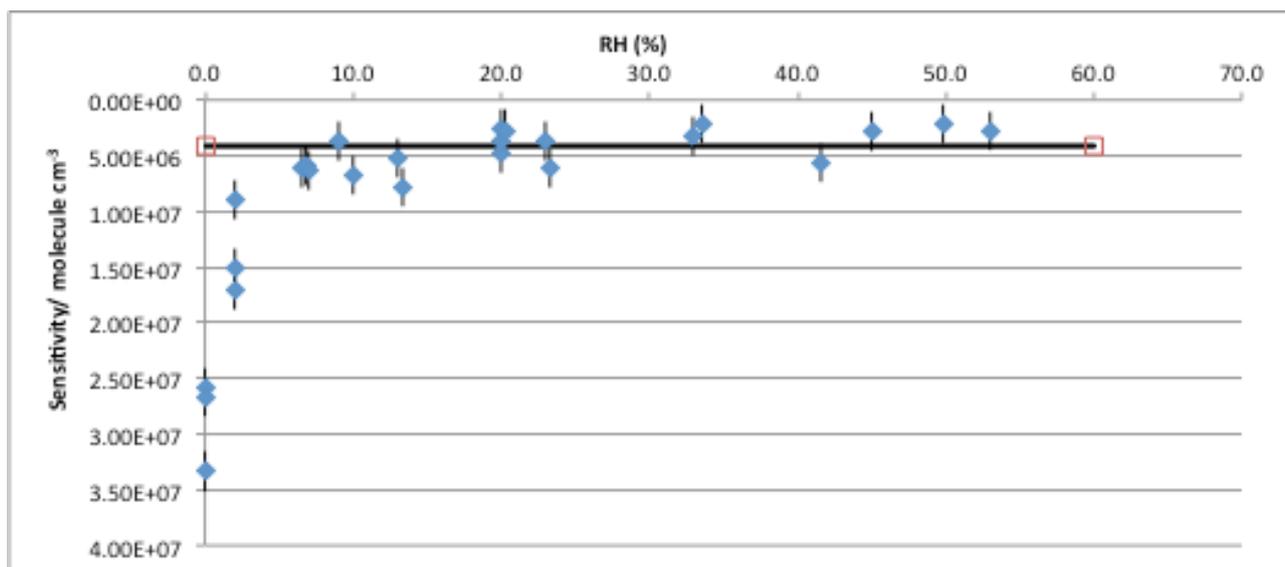
As can be seen, the sensitivity is indeed invariant with altitude, we feel that a figure does not need to be add to the manuscript.

6. Normalization to reagent ion concentration

The paragraph has been reworded so that it is clear that we corrected for reagent ion concentration and now reads

The sensitivity of the CIMS to formic acid (in units of counts/ppb of formic acid) was calculated as the ratio of the background corrected formic acid calibration counts to the formic acid absolute calibration factor (in units of ppb), the HCOOH formic acid signal was normalized for $\text{IO}\cdot\text{H}_2\text{O}^-$ counts to remove variance caused by changes in reagent ion signal.

The sensitivity of the CIMS mass spectrometer as a function of RH is shown below. At $\text{RH} > 10\%$ the sensitivity is independent of RH. At no point during the flight do we encounter RH less than 10%, thus we can ignore the impact of RH on sensitivity.



7. Calibration and Background Details

Details of the calibration addition and the frequency of background determinations have now been included with the following two sentences

Calibration gas is delivered via 1/8" diameter PFA tube to the acid-scrubbed air (3/8" tubing) about 3 cm before the 3-way valve. Total inlet flow was measured and no clear difference between background/calibration flow and flow in sampling mode was observed, and the pressure drop across the scrubber is hence minimal.

The background was determined in-flight every thirty minutes. The average difference between consecutive backgrounds was 30 pptv.

8. More complete review of CIMS instrumentation.

We have included the references that the referee suggests and the manuscript now includes this paragraph

Proton transfer reaction mass spectrometry has been used for the detection of organic acids, however it has LODs of the order of ppb (de Gouw et al., 2003). Whereas, Negative ion Chemical ionization mass spectrometry (CIMS) has proven to be a powerful method for sensitive and selective measurements of organic acids at the ppt level. (Amelynck et al., 2000, Crouse et al., 2006, Paulot et al., 2000). More recently, Veres *et al.* (2008), Roberts *et al.* (2010), Roberts *et al.*, 2011, Bertram *et al.*, (2011) have shown that chemical ionisation mass spectrometry can be used to

selectively detect gas-phase organic acids with a limit of detection below 0.1 ppbv for 1s measurements of formic acid. The rapid time response of CIMS is particularly well suited for airborne measurements, and this study focuses on the development of a negative ion chemical ionisation mass spectrometer (CIMS), utilizing I^- , as a method for the on-line measurement of carboxylic acids on an airborne platform.

9. UT measurements.

Whilst we recognize that the measurements of Reiner et al., are in the UT region, they are the only other measurements on the altitude profile that have been reported in the literature that we can compare to, thus we feel that this section should remain.

10. Emission rates

The emission rates used are directly quoted from the Grojean paper, we refer the reader to the original paper for the details of area etc.

11. Figures

The captions have been altered to include the extra information requested. Figure 3 is not more informative on a log scale, and in figure 5 the dots represent concentration, they will merge so that data gaps can not be seen. However, figure 5 in conjunction with figure 4 provides the necessary information.

References

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