

## ***Interactive comment on “***

# **Airborne observations of formic acid using a chemical ionisation mass spectrometer” by M. Le Breton et al.**

### **Anonymous Referee #2**

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#### Summary:

This work presents a chemical ionization mass spectrometry (CIMS) methodology for observing formic acid mixing ratios in the atmosphere. In situ formic acid observations from instrumentation deployed on the FAAM BAe-146 aircraft platform are presented. Data are interpreted using simulations from a ‘trajectory model’ which includes ground based emission inventories and standard chemical mechanisms. General impression:

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I believe the instrumental methodologies presented in this work will find general utility in the atmospheric chemistry community. However, I find the presentation of the modeling effort and comparison with observations to be quite weak, not informative, and in need of either substantial improvement or complete removal from the paper. I suggest removal of the modeling section and a tightening up and perhaps even expansion of the instrumental section will shape this work into a valuable contribution to the AMT literature archive.

#### Comments on modeling section:

I will not give specific comments on the modeling section, but only point out some general issues.

My understanding of recent observational and modeling work (e.g. deGouw, et. al, JGR, 2005, and Paulot, et. al, ACP, 2011) is that direct anthropogenic emissions of formic/acetic acids is very small in comparison to in situ production (and even other sources of direct emissions), whereas here, the authors argue for large, direct, missing anthropogenic source of formic acid, without providing much evidence.

Figure 8 (a repeat of figure 4) contains only 4 model data points, along the flight track. As the model is a trajectory model, a proper comparison should use continuous model data for the entire flight track.

The authors focus on what they deem to be three distinct plumes encountered along the flight track. However, from the data, it is not evident that there are distinct plumes, and other support is not convincing. To convince the reader of this conjecture, a figure of tagged-model CO on top observations showing very good agreement (or something similar) would be required.

Very troubling is the statement (P5817, L23-25) that formic acid observations do not correlate with CO, NO<sub>x</sub>, or O<sub>3</sub>. CO lifetime is very long relative to the transport timescales discussed here, and is a direct emission from anthropogenic sources,

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whose enhancement should be readily observable in the anthropogenic plumes encounters mentioned in this study. If formic acid in this region is dominated by direct (or even secondary) anthropogenic emissions, one would expect to see a good correlation between CO and formic acid. What is the correlation in the model between CO and formic acid?

General comments:

Closer attention to details of writing would improve this work.

Text could be improved by making sure each paragraph addresses a single idea, which is clearly stated in the first sentence.

Discussion of previous formic acid observations seem to be scattered throughout the text. Suggest grouping these into only two locations: 1) discussion of different methods, similarities/differences and advantages/disadvantages to current methodology and broadening discussion to all instrumentation methodologies; and 2) comparison of atmospheric formic acid observations.

References need significant attention as several are missing and others are not correct.

Working from print version specific/technical comments:

P5808, L12: lower case 'o' in ozone

P5809,L6-8: This statement is not generally true, e.g. unsaturated acids can have a very fast OH reaction rate constant, some acid readily photolyze, in the UT OH reaction can be major loss mechanism even for less reactive acids. Suggest removal of this sentence.

P5809, L18,20,21: As written these emission rates have no absolute meaning for the reader, as the emission area dimension is not defined. Please define.

P5810, L8: No Paulot, et. al, 2010 in reference list. Please add.

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P5810, L6-19: This paragraph needs cleaning up. Start with a topic sentence which clearly states the idea of the paragraph. Last two sentences seem to state the same things.

P5810, L21-24: use phrase 'organic acids' as opposed to just 'acids'. Need more complete review of previous work in this area: Amelynck, C, et. al, Int. J. Mass Spec., 2000; Crouse, et. al, Anal. Chem., 2006; Paulot, et. al, Atmos. Chem. Phys., 2009. PTR-MS (also CIMS technique) has provided reasonable acetic acid observations (e.g. deGouw et. al, J. Geophysical Res. Atmos., 2003)

P5811, L21: '...inlet flow of 13l...' does this mean 13 liters? A flow rate should have dimensions of volume/time.

P5811, L35: What is the sample flow through the 380 um orifice? Does the upstream pressure (and thus the flow through the orifice) vary with ambient pressure? If so, how was this flow variation corrected for in the data workup?

P5811, L28: State how flow rates controlled.

P5811, L28: Need to answer the following in the text. What are concentrations of the individual components (CH<sub>3</sub>I/H<sub>2</sub>O/N<sub>2</sub>) of the gas mixture? Is this mixture generated in real time from liquid components or is it premixed and stored in a cylinder?

P5812, L3: State size of this pinhole.

P5812, L7: Need to state exact pressure of CDC chamber, as this is important if someone were to replicate this methodology.

P5812, L22: What is distribution of I-, I·H<sub>2</sub>O, and higher I- water clusters (I·(H<sub>2</sub>O)<sub>n</sub>) in the ion-molecular reaction region? Can you actually know this, because of CDC redistribution? How stable is this distribution over the course of a flight? Likely, the reactivity towards formic acid changes with the number of H<sub>2</sub>O molecules clustered to I-. Even if water mixing ratio in the ion molecular region is well-controlled, the clustering distribution will be highly temperature dependent. Was IMR temperature-controlled?

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Discussion of these topics should be included in the text.

P5813, L17-20: These sentences appear to say the same thing.

P5813, L20-21: This statement should be supported with a figure.

P5813, L22-24: This statement is unclear. Please state the actual range of calibration factors, along with mean and stdev of calibrations.

P5813, L25-28: While it is useful to state the absolute sensitivity (counts s<sup>-1</sup> pptv<sup>-1</sup>) to give reader a sense of precision), when calibrating and working up data, the standard practice is to use a signal which is normalized by the reagent ion count-rate, where signal and reagent ion signal are monitored in rapid succession. This removes the variance caused by changes in reagent ion levels. This paragraph implies that normalization for reagent ion signal was not done. If not, this should be explained in the text.

P5814, L1-5: Need to specify where the calibration gas was added to measure instrument response. Though 2" steel tube? Smaller inlet tube? If calibration gas did not take the same flow path as ambient gas, then the measured response time may not be the ambient response time. This should be discussed.

P5814, L7-15: It is my impression that the Roberts and Veres studies used the same method/instrument? Also, Roberts, et. al, 2010 is not in the reference list.

P5814, L25-28: This is an awkward sentence. Suggest rephrase.

P5815, L1-7: State calibration/zero frequency. Also, zero stability should be discussed in terms of whether the frequency is adequate to capture the stability. When zeroing/calibrating, how was the scrubbed ambient flow into the instrument guaranteed to be the same as the ambient flow. Was there a pressure control system used to control the pressure in the heated inlet? One might expect a pressure drop across the scrubber.

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P5816, L1: Detection limit stated here is different than on P5814, L1. Which is correct?

P8518, L13-14, Fig. 7: formic acid data are shown up to 2300m, while calibration was only confirmed up to 3000 ft? Is this a typo, or is data outside of calibration range? Related: measurements should be reported in SI units (ie convert 'ft' to 'm').

P5818, L21-23: This statement about AMS in future experiments is out of place and should be removed.

P5819, L1-4: The Reiner work was in a much different section of the atmosphere (UT) and the trend in formic acid in this region is not necessarily related to the trend in the same species in the lower (0-3000m, mostly boundary layer air) atmosphere. Thus, agreement in the trends between these observations does not mean much, if anything (i.e., very different processes are occurring in the boundary layer). Also, I find stating the concentrations observed in the Reiner study to have no bearing to the current work. Suggest removing the whole paragraph.

P5821, L4-6: This statement is not accurate (see Paulot, et. al, ACP, 2011 – Wennberg group made formic/acetic/propanoic acid observations from aircraft campaigns during MILAGRO/INTEX-B). Rephrase.

Figure 2: State the full width half max (FWHM) of the peaks somewhere, perhaps in the caption. Comment on non-identified peaks.

Figure 3: This might be more informative if displayed on a log scale.

Figure 4: Remove lines when there is no data displayed (in transit and cal/zero periods)

Figure 5: What does the dot size mean? Altitude? In my opinion this makes the figure difficult to read. I cannot see the no-data gaps shown in Figure 4. Suggest using a constant dot size, zooming in on data more, and placing some time labels on the flight track to link it with figure 4.

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Interactive comment on Atmos. Meas. Tech. Discuss., 4, 5807, 2011.

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