

## ***Interactive comment on “Investigation of secondary formation of formic acid: urban environment vs. oil and gas producing region” by B. Yuan et al.***

### **Anonymous Referee #1**

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#### Review of

Investigation of Secondary Formation of Formic Acid: Urban Environment vs. Oil and Gas Producing Region

by B. Yuan et al.

#### General Comments

This manuscript reports a comprehensive analysis by a productive and well-respected group of researchers that addresses a topic relevant for publication in ACP.

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In general, the manuscript is well written and the interpretation of results thorough. However, the description of methods used to parameterize and run the box model is rather cryptic. Since interpretation of the simulated results is central to the overall analysis, the approaches employed to initialize the model runs and to account for losses of reactant species over the course of the simulations should be reported in sufficient detail for readers to understand what was done. In addition, the implications of variability in lifetimes against deposition among constituents should be discussed and the logic behind the approach used to dilute the model air parcels justified. Finally, as mentioned below, I would have thought that evaluating the distinct results for the 2012 and 2013 campaigns at UBWOS under presumably similar emission scenarios would provide useful insight regarding the relative importance of different sources for formic acid. It is unfortunate that the 2012 data were not evaluated in detail as part of the analysis.

After satisfactory revision to address the issues raised herein, I recommend that the manuscript be published and congratulate the authors on a nice piece of work.

#### Specific Comments

Page 24,868, lines 11-12. Given that emissions of precursors were probably similar during the 2012 and 2013 campaigns at UBWOS, it would seem that relevant information regarding the nature of secondary production of formic acid could be gleaned by explicitly evaluating differences in chemical processing during the two periods. The rationale for ignoring results from the former campaign and focusing only on those from the latter is unclear.

Page 24,871, lines 1-4. The description of how the model was parameterized and run is overly vague and should be clarified. Here, the authors refer to interpreting "... simulated diurnal profiles of ... photochemical products" including ozone, acetaldehyde, acetone. However, on the preceding page they indicate that "hydrocarbons, NO<sub>x</sub>, ozone, methane, and formaldehyde are constrained in the zero-dimensional box

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model to the average measured diurnal profiles for each campaign, and the model is run toward a diurnal steady state (DSS).” By “constrained”, do the authors mean that the average measured diurnal profiles were (1) used to initialize the model at the beginning of the simulation or (2) held constant throughout the 10-day simulation? If (1), there is no mention of replacing precursor compounds lost via reaction during the simulation. If this was not done, what are the implications for modeled results as precursors concentrations decreased over the course of the 10-day simulation? If (2), it would be helpful to explain the distinction between the “constrained” and simulated profiles of ozone and other products in the model.

Page 24,871, lines 9-15. Simple dilution via mixing with background air that contains no reactant or product species would have the same influence on all chemical constituents in the model but differential losses via deposition would not. Lifetimes against deposition vary over orders of magnitude among constituents. Lumping the influences of dilution and deposition into a single term that influences all species (or only product species?) equally is potentially problematic. Not all box models are parameterized using this approach and, indeed, some explicitly consider variability among constituents with respect to their atmospheric lifetimes against deposition. Simply varying the magnitude of this single term, as was done for the sensitivity calculated reported in Section 3.4, does not provide insight regarding the potential implications of differential variability in lifetimes among the suite of constituents considered in the model. I encourage the authors to address this issue either here or in Section 3.4.

In addition, it appears that this approach for diluting the model air parcel is based on the implicit assumption that “background air” contains no formic acid or other product species. However, formic acid and other products are ubiquitous but variable constituents of the global troposphere. Consequently, mixing representative “background air” into the simulated air parcel should not result in a proportionate decrease in concentrations of all constituents (or all product species?). What are the implications of the authors’ approach?

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Figure 1, caption. Please specify the percentiles represented by the box-and-whisker plots. In particular, percentiles depicted by whiskers vary among different applications from the upper and lower 10th to 5th to extreme values.

Page 24,873, lines 10-14. In lines 1 and 2 on this page, the authors indicate that the “likely range” in relative contributions from combustion sources will be evaluated based on the indicated range in emission ratios. However, on line 11 they report only individual values for each campaign, which presumably are based on the higher emission ratio. In addition, it appears that the symbols may not have converted properly when the text file was uploaded. I infer that what appears on my screen as “. . . -13 and -18% . . .” should be “. . . ~13 and ~18% . . .”. Assuming so, the text should read “. . . combustion sources accounted for 0% to approximately 13% of formic acid during CalNex and 0% to approximately 18% of formic acid during UBWOS 2013.” Please clarify the text for consistency. If the estimated contributions are indeed negative, then either some of the measurements are biased or the emission ratios used are not representative. Regardless, relatively large negative contributions do not provide compelling support of the conclusion that “. . . primary emissions only contributed a minor part to formic acid concentrations.” More generally, since formic acid and CO have different atmospheric lifetimes, is it reasonable to assume implicitly that emission ratios for combustion sources are conservative with respect to atmospheric processing and thus directly applicable to relative concentrations in ambient air? If not, what are the implications for interpreting these results?

Page 24,880, lines 24-26. While it is true that “. . . the sinks of formic acid during both campaigns are dominated by physical losses and that the chemical losses of formic acid are slow” this is not the case for all precursor and other product compounds most of which have much lower deposition velocities than formic acid. As noted above, it is unclear how the sensitivity of the mechanism can be reliably evaluated by adjusting all lifetimes by the same amount.

Page 24,886, lines 1 to 5. Since formaldehyde is the presumed precursor for formic

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acid produced in fogwater (e.g., Chameides and Davis, 1983), it would be appropriate to include formaldehyde in Fig. 7 and evaluate its variability relative to that of formic acid. Previous paired measurements of formaldehyde and formic acid in cloud water and interstitial air during daytime revealed no evidence for significant formic acid production via this pathway (Keene et al., 1995, JGR). Is the inferred enhancement of 4% significantly greater than 0%? To provide readers with a better perspective on overall reliability, it would be helpful here and elsewhere (e.g., Fig. 9) to include the estimated ranges in uncertainties for inferred contributions from different pathways.

Page 24,887. Since most formate and oxalate are secondary products of hydrocarbon oxidation, it is not unreasonable to assume that their concentrations in snow were correlated. However, based on their respective thermodynamic properties, the solubility of formic acid varies as a function of solution pH whereas that of oxalic acid does not. Consequently, it is reasonable to expect that the different gradients in formic acid were driven by the thermodynamics of phase partitioning as suggested by the authors. Similarly, it is reasonable to expect that the gradient in formic acid would have been largely decoupled from the corresponding concentration of oxalate in snow as indicated in Fig. 8b. The relative variability in oxalate versus that for the product of oxalate and HNO<sub>3</sub> depicted in Fig. 8 suggest that HNO<sub>3</sub> alone accounted for much of the variability in formic acid gradients. During the period 7 to 11 February, HNO<sub>3</sub> concentrations in air were relatively low and most of the formic acid gradients were negative. Conversely, during the period 13 to 16 February, HNO<sub>3</sub> concentrations were relatively high and most of the formic acid gradients were positive. It is unclear what value is added by interpreting these data based on the product of oxalate in snow and HNO<sub>3</sub> in air as opposed to HNO<sub>3</sub> vapor alone.

Page 24,889, lines 23-24. Although probably correct, the conclusion that “secondary formation was the main source of formic acid during the two campaigns” seems a bit strong in light of the fact that the production pathways considered in the model accounted for a maximum of about 50% of measured formic acid at both locations.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 24863, 2014.

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