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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 #2

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This paper describes the CIMS measured formic acid and examines the secondary formation chemistry and sink processes using box model simulations. Formic acid concentrations measured in an urban California site during the summer and in an industrial Utah site during the winter are quite similar, regardless the different atmospheric source processes and VOCs levels and photochemical activities. With updated oxidation reaction schemes in secondary formation processes and by including non-gas phase processes (with high uncertainties at present), the authors found that they can increase model predicted values, but still nearly half of formic acid is from unknown sources/chemistry. The make-ups from different processes are different at these two

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locations, due to their different VOCs and heterogeneous processes. The sink is mostly the physical loss, than chemical reactions. This is a very interesting paper that shows valuable measurements and comprehensive data analysis. This should be published in ACP. I suggest the authors make additional efforts to edit the manuscript.

While I am convinced with the sensitivity analysis results, it is not clear to me how primary formic acid (emissions) is prescribed in model. I am curious why the baseline conditions predict so low formic acid in 2013 winter in Utah. In Figure 1b, the 2012 Utah results, since there were no strong photochemical activities and no ozone formation and so presumably no secondary formation for formic acid, were mostly due to only the primary emissions and sink (around 0.5 ppb). But in Figure 4 the baseline model values (around 0.1 ppb) are much lower than the winter 2012 concentrations. I guess if you run model for 2012 conditions, the baseline would be still much lower than measurements? Does this mean that the 2012 Utah formic acid still has 80% from secondary formation.

With regard to model: Why not include NO_3 chemistry? When the model can predict aceton and CH_3CHO pretty well (Figure S4, which should be in main text) even for consecutive 5-7 days long, why are the differences between model and measurements are so large for formic acid? Related to this, formaldehyde is constrained by measurements, and I wonder why well the model can predict formaldehyde compared with measurements? I also feel the isoprene OH oxidation reaction yield for formic acid used in the updated MCM is still very low. And what is the reason you chose MCM as opposed to other models? It would be nice to show reaction schemes in detail, for example for those mentioned in the section 3.3 (with molecular structures in supplement). How is transport process described in your box model?

Fog process: the fog process only increases formic acid secondary formation 4%, as stated. This seems too small, when compared to the measured formic acid concentrations that elevated during fog events (up to 10 ppb, Figure 7) and the modeling prediction shown in Figure S6.

Snow exchange: Did you measure oxalate only? Or oxalate was the only organic acid you detected above detection limit from snow? If formate ions were very low (say, lower than detection limit), then this should indicate that snow exchange process is not important for gas phase formic acid, right? Why would nitric acid replace formic acid and other organic acids in snow (page 24877 last part)? Would nitric acid also replace oxalic acid? How does aceton interact with snow?

Page 24865, Line 5: It would be more informative if you describe the location and season of the measurements, than name (or in addition to) the field campaigns.

Page 24865: I suggest Line 13-15: "Compared to the original MCM model that included only ozonolysis of unsaturated organic compounds and OH oxidation of acetylene, when we updated yields of ozonolysis of alkenes and included OH oxidation of isoprene, vinyl alcohol chemistry, reaction of formaldehyde with HO_2, oxidation of aromatics, and reaction of CH_3O_2 with OH, the model predictions were improved up to xxx" or similarly.

Page 24866, Line 5-6. The carboxylic acids that can contribute to new particle formation are low volatility compounds. Formic acid that is too volatile (as you showed here, even it comes out from cold snow) is unlikely involved in this process.

Page 24868, Line 21: Can you explain 25% of uncertainties for CIMS, which is real high precision.

Page 24872: Isoprene is a primary compound but it does not show the spikes, and it shows diurnal variation, like formic acid.

Page 24874, Line 1. "In fact" to "However"?

Page 24874, Line 15-18: In Figure 4, the measured formic acid values do not show noontime peak, rather they show higher concentrations broadly in the PM.

Page 24876, Line 21. Remove "In addition to isoprene"?

Page 24877, Line 21: what do you mean with "equilibrium product"?

Page 24885, Line 3: "area" to "aerosol".

Table S1. 6. Please rephrase: "a long-lived missing secondary source of formic acid"

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