Response to comments from Reviewer #2

General Comments

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 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.

Reply: We thank the reviewer for the valuable comments. We considered all of the comments from the reviewer and the point-to-point response to individual comments is listed below in this file. The comments from the reviewer are shown in black. The response is shown in blue and the changes in the manuscript are shown in bold blue.

Specific Comments

1. 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.

Reply: Primary emission of formic acid is not prescribed in the box model. The box model only calculates the amount of formic acid produced from secondary formation. We compared the model results with the calculated secondary formic acid concentrations by subtracting the primary part (paragraph 6 in section 3.4). We added a description sentence in Section 2.3 to clarify this information.

We note that primary emissions of formic acid and other photochemical products (e.g. acetone) are not prescribed in the box model. The box model output will be compared to the calculated secondary concentrations by subtracting the primary part.

Before we reply to the comments about the secondary contribution of formic acid in UBWOS 2012, we need to clarify that the emission ratio of HCOOH/CO used to calculate of primary formic acid is updated in the revised manuscript using values in a recently published study (Crisp et al., 2014) (see detailed response to comment #6 from reviewer #1).

Using the latest HCOOH/CO ratio in Crisp et al. (2014) and applying the same procedure as UBWOS 2013 to calculate primary emissions of formic acid, we derive that primary emissions only account for 1.0±0.7% of formic acid concentrations in UBWOS 2012. This result is consistent with the reviewer's suggestion. The daytime maximum in the diurnal profile of formic acid in UBWOS 2012 also indicated the secondary formation of formic acid in UBWOS 2012. Although the concentrations of formic acid were lower and photochemistry was weak in UBWOS 2012, secondary formation still dominated the source of formic acid in UBWOS 2012. We added this information in Section 3.1. In the response to comment #1 of reviewer #1, we also added an explanation about simulating formic acid concentrations in the box model in UBWOS 2012.

Using the same procedure, we determine that primary emissions from combustion sources accounted for 1.0±0.7% of formic acid in UBWOS 2012, although photochemistry was weaker in 2012 compared to 2013.

2. With regard to model: Why not include NO3 chemistry? When the model can predict acetone and CH3CHO 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?

Reply: NO_3 chemistry was included in all of our box model runs. Measured NO_3 an N_2O_5 concentrations by cavity ringdown spectroscopy (CRDS) are used as constrains in the model. This information is added in the Measurements and Method section in the revised manuscripts.

A cavity ring-down spectroscopy system was used to detect nighttime NO_3 and N_2O_5 in the atmosphere (Dubé et al., 2006).

We agree with the reviewer that acetone and CH_3CHO are predicted well in the emission-based box model for the UBWOS 2013. The good performance of acetone also helped us to use HCOOH/acetone ratio as a metric to evaluate the performance of the box model to formic acid (Section 3.4). The differences between model and measurements for formic acid are the main topic of this manuscript. We showed that other processes (aerosol-related reactions, fog events and air-snow exchange) can partially explain the large differences, but half of the formation sources for formic acid are still missing.

Formaldehyde is constrained in the box model using the measurements. It has been shown that formaldehyde is underpredicted in both box model and WRF-Chem, compared to measurements in UBWOS 2013 (Edwards et al., 2014;Ahmadov et al., 2014), which may be due to either direct emissions or incomplete model chemistry. Since formaldehyde can be an important radical source in the box model, we decided to use formaldehyde measurements as constraint in our box model.

The yield (10%) of formic acid from OH oxidation of isoprene used in this study is from the study of Paulot et al. (2009). This work (Paulot et al., 2009) is the only chamber study reporting formic acid yield from OH oxidation of isoprene. More studies on the yield of formic acid from OH oxidation of isoprene (and other precursors) are needed to reduce the uncertainties in the model performance.

Most of the newly added or revised reactions have been described in Tables S2 and Table S3 in the supplement. Some of the revisions are straightforward (such as formic acid is just added as an additional products from aromatics oxidations) and they are not listed out in Tables S2 or Table S3.

It is impossible to treat transport explicitly in a box model. We used a single loss term to represent all of the physical losses, including dilution by background air and depositions. Dilution processes can be due to gas diffusion, entrainment flux and transport of clean air masses from upwind direction. We also investigated the effects of varying the settings of the physical loss rate in the box to modeled formic acid (Section 3.4). We conclude that the ratio of HCOOH/acetone is a good metric of the model performance on formic acid modeling, as the ratio does not change much with the settings of the physical loss rate.

In this study, MCM v3.2 is used as the chemical mechanism in the box model. MCM (Master Chemical Mechanism) is a state-of-the-art near-explicit chemical mechanism for atmospheric chemistry (Jenkin et al., 2012) and it is widely used in the community to study atmospheric chemistry. As we have detailed volatile organic compounds measurements in both UBWOS 2013 and CalNex, using these measurements as constraints is both easier and more accurate for MCM than other lumped chemical mechanisms. Since most of the formation pathways of formic acid are newly added or revised in the MCM v3.2, using other chemical mechanism with consistent modifications would give similar model results.

Besides box model, 3-D photochemical models are also widely used to investigate secondary formation of photochemical products. For example, a WRF-Chem study on simulating ozone chemistry in UBWOS 2013 was published in the same special issue in ACPD (accepted in ACP earlier) (Ahmadov et al., 2014). Ahmadov et al. (2014) showed that emissions of methane and other VOCs are too low in the bottom-up emission inventories. Modeling the “cold pool” meteorology in Uintah Basin was also challenging in UBWOS 2013 (Ahmadov et al., 2014). However, as formic acid is specifically focused on in this study, we decide to take advantage of the flexibility, the detailed chemistry and easier constraints using measurements from a box model.

3. 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.

Reply: Thanks for the comments. The reported 4% is the campaign-average contribution from fog processes. We agree with the reviewer that fog contribution can be much larger in some certain periods (e.g. the morning of Feb. 7, Figure 7 in the manuscript). But fog processes were only important in the mornings of several days, which are still a small part of the whole period in a 4-week campaign. This sentence is added to the revised manuscript.

This contribution is not a large source for formic acid for the four-week campaign, but fog formation accounted for significant formic acid concentrations in certain periods (e.g. the morning of Feb. 7).

4. 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 acetone interact with snow?

Reply: Yes, we only measured oxalate for snow samples. Formate ion in snow samples was not measured during the UBWOS 2013 campaign. Since nitric acid is a stronger acid than formic acid and the reaction $HNO_3 + HCOO^- = NO_3^- + HCOOH$ (Δ_rG^o=-41 kJ/mol) (Lide, 2005) is thermodynamically favored, deposition of nitric acid to snow surface may display formate in the snow to produce formic acid, which can return to the atmosphere. Based on the thermodynamic data, the reaction of nitric acid with oxalate ions is also thermodynamically favored (Δ_rG^o=-50 kJ/mol) (Lide, 2005). We added this sentence in the revised manuscript to clarify this.

"…deposition of nitric acid to the snow surface and the acid displacement reactions due to nitric acid, which is thermodynamically favored (HNO_3 + $HCOO^-$ = NO_3^- + HCOOH, Δ_rG^o=-41 kJ/mol) (Lide, 2005), may play important roles in the air-snow exchange of formic acid (and other organic acids).

Some studies reported that acetone can be also produced from snow under sunlight (Gao et al., 2012). But we did not observe any significant gradient for acetone during the UBWOS 2013 campaign. Thus, we conclude that air-snow exchange contributed at most minor contribution to acetone concentrations in UBWOS 2013.

5. 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.

Reply: Thanks for the comment. We added the names of the two sites (Pasadena and Uintah Basin) in the abstract. The measurement seasons for the two campaigns were already included in the ACPD version.

6. 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 HO2, oxidation of aromatics, and reaction of CH3O2 with OH, the model predictions were improved up to xxx" or similarly.

Reply: Thanks for the comment. We have changed this sentence according to reviewer's comments.

7. 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.

Reply: We agree with the reviewer. We have changed the sentence to: "**Some higher carboxylic acids are proposed to enhance new particle formation…**".

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

Reply: The 25% uncertainty for CIMS is the accuracy, not the precision. The uncertainties in the CIMS measurements are due to: concentrations of formic acid from the permeation tube used for calibration (10%), the errors associated with calibration procedures and data reduction (10%), and background correction errors. The background correction errors are mainly due to the variations of background signals (typically 0.3 ppb) (Bertram et al., 2011). We linearly interpolate the background measurements measured every 2-3 hours to each ambient measurement data points to obtain the background signals. Thus, variations of background signals can also affect the measurement errors.

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

Reply: Measured isoprene was very low in UBWOS 2012 (0.4± 2.3 ppt) (isoprene was not measured in UBWOS 2013) (see also Figure 3). The low concentrations of isoprene at Horse Pool site during UBWOS campaign are due to: (1) very low emissions from plants during the winter; (2) Oil and gas extraction activities are not a source for isoprene (Warneke et al., 2014). The measured diurnal profile of isoprene in UBWOS 2012 is shown in the graph below. No clear diurnal variation was observed for isoprene in the UBWOS 2012.

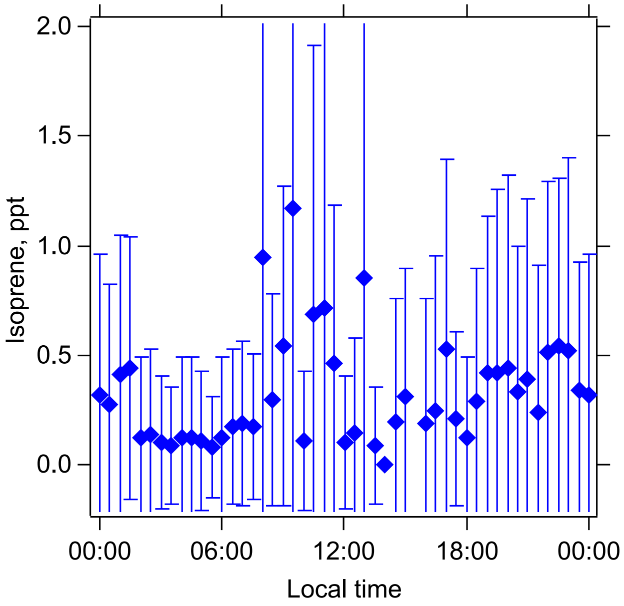

Fig. R1. Diurnal profile of measured isoprene at Horse Pool site in UBWOS 2012. The error bars in the graph indicate the standard deviations.

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

Reply: Done.

11. 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.

Reply: We changed “noontime peaks” to “broad afternoon peaks”.

12. Page 24876, Line 21. Remove “In addition to isoprene”?
Reply: Corrected.

13. Page 24877, Line 11: what do you mean with “equilibrium product”?
Reply: The sentence has been rephrases:
Reactions of HOCH2OO, a product from the reaction of formaldehyde (HCHO) with HO2 radicals

14. Page 24885, Line 3: “area” to “aerosol”.
Reply: Corrected.

15. Table S1. 6. Please rephrase: “a long-lived missing secondary source of formic acid”
Reply: Corrected to “**long-lived missing precursors of formic acid**”.

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