# Response to comments from reviewers

## Reviewer #1

**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. 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.

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. 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.

Reply: We thank the reviewer for the comments. We agree with the reviewer that emissions of hydrocarbons and NOx are very similar between the UBWOS 2012 and UBWOS 2013 campaign, but the chemistry was much slower in 2012. The mainly differences were shallower boundary layer height and increased photolysis frequencies due to the higher snow albedo in 2013 (Edwards et al., 2014). The only difference in the setup of an emission-based box model between 2012 and 2013 would be the magnitudes of photolysis frequencies. This difference in box model only results in longer photochemical processing times, whereas the modeled ratio of formic acid to acetone would remain the same. The emission-based box model shown in Section 3.4 (and Fig. 6) also show that the modeled ratio of formic acid to acetone does not change much over the period of more than 1 week simulation with significantly varying photochemical processing time. We added this information in Section 3.4 in the revised manuscript. **As emission compositions of hydrocarbons were not found to be different between**

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**UBWOS 2012 and UBWOS 2013, the performance of the emission-base box model can also represent the conditions in UBWOS 2012. As shown in Fig. 6, we observe a similar explainable fraction of formic acid in UBWOS 2012 as that in UBWOS 2013 by the box model.**

2. 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, NOx, ozone, methane, and formaldehyde are constrained in the zero-dimensional box 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.
Reply: We apologize for the confusion here. The sentence *"…the simulated diurnal profiles of formic acid and other photochemical products (e.g. ozone, acetaldehyde, acetone) change little compared to the previous day"* should not contain ozone, since ozone is constrained in the box model using measurements. The correct sentence should be **"…the simulated diurnal profiles of formic acid and other photochemical products (e.g. acetaldehyde and acetone) change little compared to the previous day".** We changed this in the revised manuscript.
     In this study, the average measured diurnal profiles are held constant throughout the 10-day simulations in the box model for those constrained species. This information is added to the revised manuscript.
   The box model runs every step at 10 min interval. After the box model finishes one 10-min step, the concentrations of constrained species are replaced using the measurements before the box model runs another step. Thus, there is no difference between the constrained profile and model output for ozone and other constrained photochemical products (e.g. formaldehyde). We apologize again for the confusion due to our inconsistent description in the two sentences mentioned by the reviewer.
     A new graph of the time series of modeled formic acid in a 10-day simulation for UBWOS 2013 is added to Fig S2 (A). The added graph will be helpful to understand the diurnal steady state (DSS) method and how we compare modeled and measured concentrations.

3. 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

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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.

Reply: We thank the reviewer for the comments. We agree with the reviewer that lifetime against deposition can vary significantly among different species. Based on the parameterization of deposition velocity (Wesely, 1989), the deposition rate of formic acid is likely faster than acetone, since formic acid is more soluble. If a higher physical loss rate is used for formic acid than acetone in the box model, the modeled formic acid to acetone ratio would be lower, which means that the missing source of formic acid is even larger. A discussion about the potential larger deposition velocity for formic acid and the effect on evaluating the box model performance is added in the revised manuscript. **We acknowledge that the treatment of dilution and deposition in the box model by combining the two terms and assuming the same physical loss rate for different species may affect the modeled slopes of formic acid to acetone. (1) The background air that dilutes modeled air parcel in the box model contains no formic acid and acetone. A test simulation that assumes the modeled air parcel is diluted by background air with 0.1 ppb of formic acid (Paulot et al., 2011) and 0.5 ppb of acetone (Hu et al., 2013) for UBWOS 2013 is shown in Fig. S5. Very small changes of the simulated slope of formic acid versus acetone are observed (~4%), compared with the simulation assuming background air without formic acid and acetone. (2) Deposition velocities for various species can be different. Based on the parameterization of deposition velocity (Wesely, 1989), the more soluble formic acid likely has a faster deposition rate than acetone. Accounting for this difference in deposition velocities, the modeled slope of formic acid versus acetone would be even lower than those shown in Fig. 6.**

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?

Reply: We thank the reviewer for the comments. The concentration of a species X due to dilution processes can be parameterized as (Mckeen and Liu, 1993):

$$\frac{dX}{dt} = -K(X - X_B)$$

X and $X_B$ are concentrations of the species and concentration of the species in the background air. K is the mixing coefficient. In this study, we assume that formic acid and other products (e.g. acetone) are mixing with background air without formic acid and acetone. This assumption was reasonable for this study, since concentrations of formic acid and other products were much higher than background concentrations in both CalNex and UBWOS 2013. We agree with the reviewer that mixing with non-zero background air would not result in exactly proportionate decreases in the concentrations for different species, i.e. the ratio of formic acid to acetone from the box model would

change slightly. A simple test simulation assuming model air parcel diluted by background air with 0.1 ppb formic acid (Paulot et al., 2011) and 0.5 ppb acetone (Hu et al., 2013) for UBWOS 2013 are shown in the Figure below. Very small changes in the simulated slope of formic acid versus acetone are observed (~4%). We do observe the change of the offset as the result of non-zero background air, but the slope is the parameter that is used to compare with the measured enhancement ratio of formic acid to acetone. We added a new paragraph in Section 3.4 to discuss this concern, as detailed above in the response to comment #3.
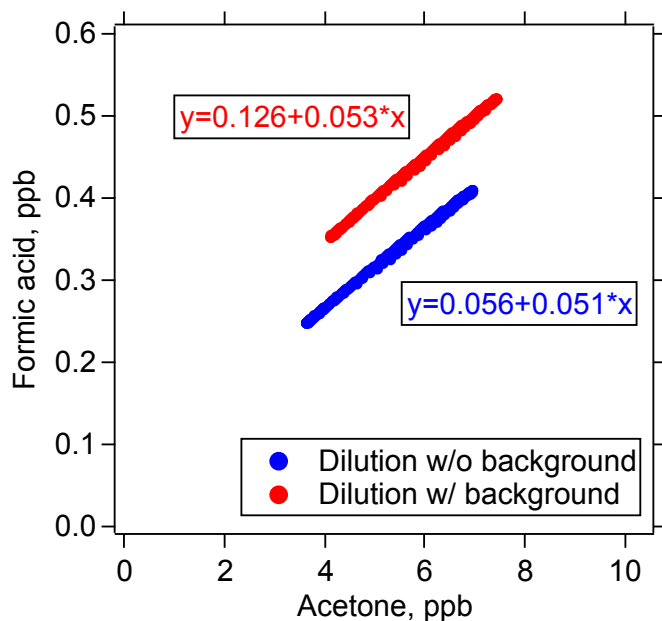


Fig. 1. Scatter plot of formic acid versus acetone from simulations with different settings of physical loss rates in the box model: dilution by background air with no formic acid and acetone associated with zero initial concentrations for the two species; dilution by background air with 0.1 ppb of formic acid and 0.5 ppb of acetone associated with the initial concentrations as in background air.

5. 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.

Reply: We thank the reviewer for the comments. A new sentence is added to caption of Figure 1.

**The boxes denote the central 50% of the data (25-75 percentile), and the bars within the box indicate the median value. The ends of the whiskers show the maximum and minimum of the data.**

6. 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

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accounted for 0% to approximately13% of formic acid during CalNex and 0% to approximately18% 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 on 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?

Reply: We thank the reviewer for the comments. We apologize that the percentages from primary emissions in the ACPD version were not accurately presented. The correct sentence should be **"...accounted for 0-13% and 0-18% of formic acid in CalNex and UBWOS 2013…".** We also noticed that there are similar errors in Section 3.5 about the contribution from heterogeneous reaction of aerosol. The two errors are both corrected in the revised manuscript.

Besides the error, we also change the calculation of primary emissions to formic acid in the revised manuscript. A new study (Crisp et al., 2014) on primary emissions of formic acid from vehicles appeared after this manuscript was published in ACPD. Crisp et al. (2014) reported the measurements of formic acid emissions factors and emissions ratios of HCOOH/CO from eight light duty gasoline vehicles. This study provides the direct measurements of formic acid emissions from gasoline vehicles with current control technology and it is believed to be more reliable than other previous direct measurements conducted more than a decade ago or those emission ratios inferred from ambient measurements with significant secondary formation (Table 1).

Using the reported values in Crisp et al. (2014), we re-calculated the contributions of primary emissions to formic acid concentrations in UBWOS 2013 and CalNex. The revised calculation indicate that emissions from combustion sources only accounted for $0.46\pm0.32\%$ and $0.24\pm0.17\%$ of formic acid in CalNex and UBWOS 2013, respectively. The two values are smaller than the values shown in the version published in ACPD. As a result of this modification, the explained percentages from the box model, missing production rates of formic acid and some other terms also changed a little bit (see Table 3). All of these small changes do not affect the conclusions we made in the ACPD version.

The rate constant of OH with formic acid and CO are $4.5\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $2.0\times10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (298 K, ambient pressure), respectively. The lifetimes of the two compounds in the atmosphere are both longer than 2 weeks. The ratio of HCOOH/CO only changes by about 4% after 1 day of OH exposure at $1\times10^6$ molecule cm$^{-3}$ (the modeled 24-hour average OH concentrations are $1.5\times10^6$ molecule cm$^{-3}$ in CalNex and $3.0\times10^5$ molecule cm$^{-3}$ in UBWOS 2013). Thus, it is reasonable to assume that the HCOOH/CO ratio is conserved with respect to atmospheric processing on the relevant time scales of the UBWOS and CalNex campaigns, which are both sampling air masses near the emission source.

7. 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 be 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.

Reply: We thank the review for the comment. In the manuscript, the sentence "*the sink of formic acid is dominated by physical losses*" is used to explain why the physical loss rate has a large effect on the modeled concentrations of formic acid, i.e. a factor of 2 higher physical loss rate reduces the modeled formic acid by a factor of ~2. Other more chemically reactive species, e.g. acetaldehyde, are less affected by the setting of physical loss rate in the box model.

We agree with the reviewer that deposition velocities of formic acid might be higher than for hydrocarbons and acetone. However, several comments need to be made: (1) Hydrocarbons and other constrained species (ozone, formaldehyde) are constrained in the box model using their measured values, and thus the concentrations of these species are not affected the setting of physical loss rates. (2) Acetone: the enhancement ratio of formic acid to acetone is used to evaluate the performance of box model. As shown in the response to the comments #3, higher deposition velocity for formic acid than acetone would decrease the enhancement ratio of formic acid to acetone. We added several sentences in Section 3.4 to address this potential issue in the box model (see added sentences in the response to comment #3).

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

Reply: We thank the reviewer for the comments. Measured time series of formaldehyde is added in Fig. 7 in the revised manuscript. We observed similar time variations of formaldehyde as formic acid during the fog event on Feb. 7, 2013. However, it is not straightforward to evaluate the importance of formaldehyde as precursor for formic acid in fog water, because liquid phase concentrations of formaldehyde and formate were not measured during the UBWOS 2013 campaign. Since formic acid, acetic acid and formaldehyde are all more soluble in water than acetaldehyde and acetone (Sander, 1999), the different behaviors of higher soluble and lower soluble species may reflect the dynamic absorption and release processes for these highly soluble species (formic acid, acetic acid and formaldehyde) to (from) fog droplets in the fog event. The information about formaldehyde during the fog event is added to the revised manuscript.

**Time variations of formaldehyde are similar with two carboxylic acids, but different from acetaldehyde and acetone. This may reflect the dynamic absorption and release processes for these highly soluble species (formic acid, acetic acid and formaldehyde) to and from fog droplets in the fog event. Due to the lack of chemical**

**measurements of fog water, we are not able to conclude whether formaldehyde contributes to formic acid enhancement during the fog events (Chameides and Davis, 1983;Keene et al., 1995).**

We determine the uncertainty of the estimate of the fraction from fog events from the uncertainties of the fits in Fig. 6. The best estimate for fog events contribution is calculated to be 4±7%. The estimated contribution is minor, but fog events can be very important in certain periods, as the other reviewer pointed out.

The uncertainty in the estimate of the contribution from air-snow exchange is also added in the revised manuscript. It is not possible to derive the best estimates for aerosol-related reactions and the possible ranges of the contributions are given in the manuscript. The uncertainties from the box model are discussed in the Section 3.7. We stated that the gas phase reactions in the box model are associated with large uncertainties. Thus, the upper limits are used to determine the fractions of many formation pathways in the production of formic acid. We also proposed that more work on the pathways of formic acid would be very helpful to reduce the uncertainties in our understanding of secondary formic acid sources.

9. 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 HNO3 depicted in Fig. 8 suggest that HNO3 alone accounted for much of the variability in formic acid gradients. During the period 7 to 11 February, HNO3 concentrations in air were relatively low and most of the formic acid gradients were negative. Conversely, during the period 13 to16 February, HNO3 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 HNO3 in air as opposed to HNO3 vapor along.

Reply: We tried to use measured $HNO_3$ concentrations to explain the gradient of formic acid (see the updated Fig. 8 below). The correlation between the gradient of formic acid and $HNO_3$ concentration was low (R=0.21), similarly to the correlation between the gradient of formic acid and oxalate in the snow (R=0.20). However, the correlation of gradient of formic acid with the product of oxalate in the snow and $HNO_3$ in ambient air significantly improved (R=0.58). Thus, the new investigation of $HNO_3$ concentration with formic acid gradient does not change our statement in the ACPD version: deposition of $HNO_3$ to snow and displacement reaction between $HNO_3$ and formate may be a source of formic acid in the atmosphere.

The updated Fig. 8 is included in the revised manuscript. The correlation information of $HNO_3$ concentration with the gradient of formic acid is also added in the revised manuscript.

**"As shown in Fig. 8, neither time variations of oxalate in the snow nor nitric acid**

**concentrations in ambient air correlated well with the concentration gradients of formic acid (R=0.20 and R=0.21, respectively), …"**
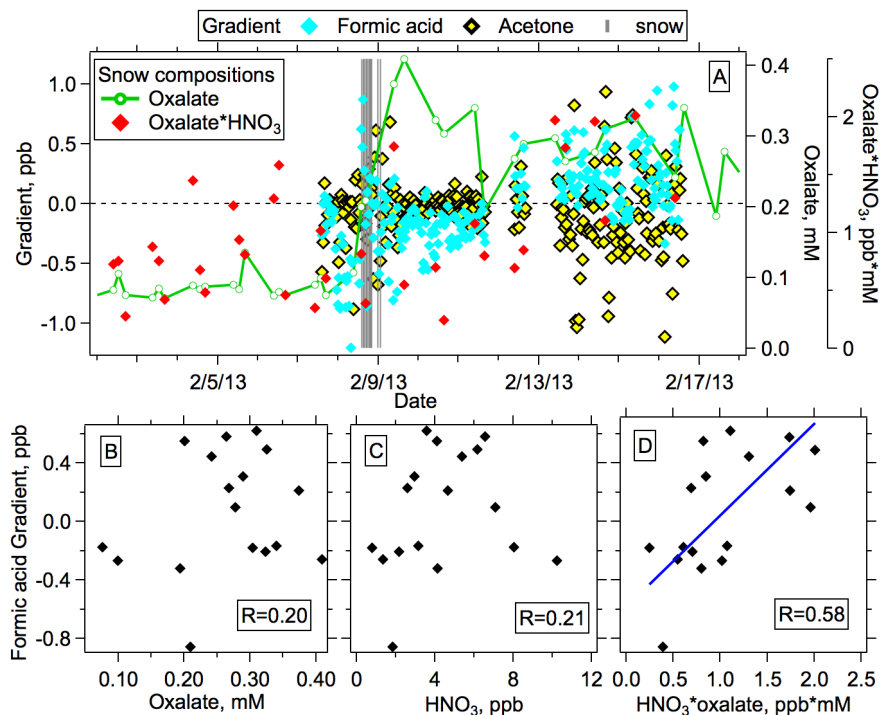


Fig. 2 (A) Time series of concentration gradients of formic acid and acetone during UBWOS 2013. Time series of oxalate measured in melted snow water and the product of oxalate in the snow and nitric acid (HNO$_3$) in ambient air are also shown. The vertical black bars indicate periods with snow fall. (B) Scatter plot of the concentration gradient of formic acid versus oxalate in the snow. (C) Scatter plot of the concentration gradient of formic acid versus nitric acid concentration in ambient air. (D) Scatter plot of concentration gradients of formic acid versus the products of oxalate in the snow and nitric acid in ambient air. The blue line is the linear regression to the data points.

10. 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.
Reply: We thank the reviewer for the comment. The conclusion that "secondary formation was the main source of formic acid during the two campaigns" is not derived from the results of box model simulations. Based on the diurnal profile analysis in CalNex (Veres et al., 2011) and several pieces of evidence from the UBWOS 2013 (lack of concentration spikes, multi-day accumulation patterns and enhancement of UBWOS 2013 over UBWOS 2012), we concluded that formic acid is dominated by secondary sources in the two campaigns (paragraph 2 in section 3.1). We also used the reported emission ratios of formic acid to CO from primary sources in the literature to estimate the fraction of formic acid from primary emissions and the same conclusion are inferred (paragraph 3 in section 3.1).

**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).

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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

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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 $HNO_3 + HCOO^- = NO_3^- + HCOOH$ ($\Delta_rG^o$=-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 ($\Delta_rG^o$=-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 ($HNO_3 + HCOO^- = NO_3^- + HCOOH$, $\Delta_rG^o$=-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.
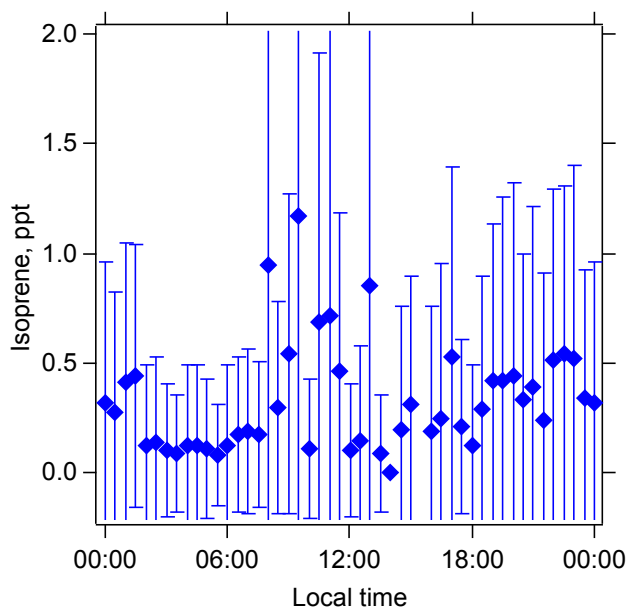


Fig. R1. Diurnal profile of measured isoprene at Horse Pool site in UBWOS 2012. The error bars in the graph indicate the standard deviations.

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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