# Response to comments from 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 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 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.

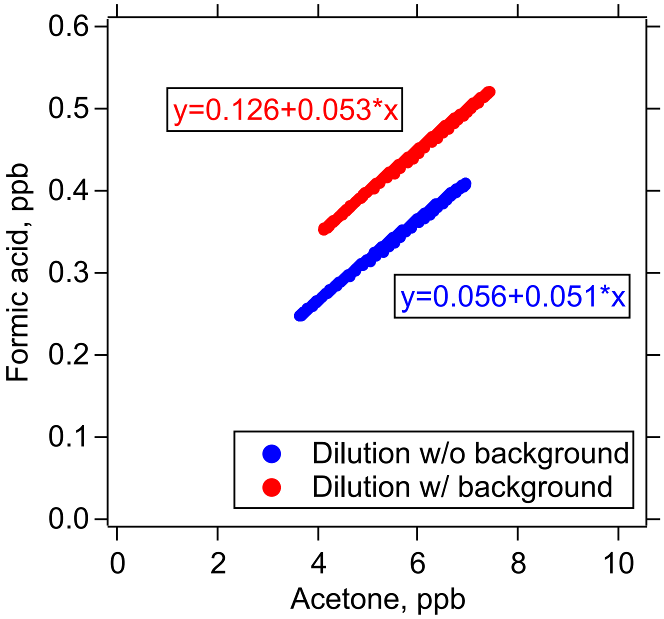

Fig. 1. Scatter plot of formic acid versus acetone from simulations with different settings of physical loss rates in the box model: dilution by background air with no formic acid and acetone associated with zero initial concentrations for the two species; dilution by background air with 0.1 ppb of formic 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 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±0.32% and 0.24±0.17% 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), …”**

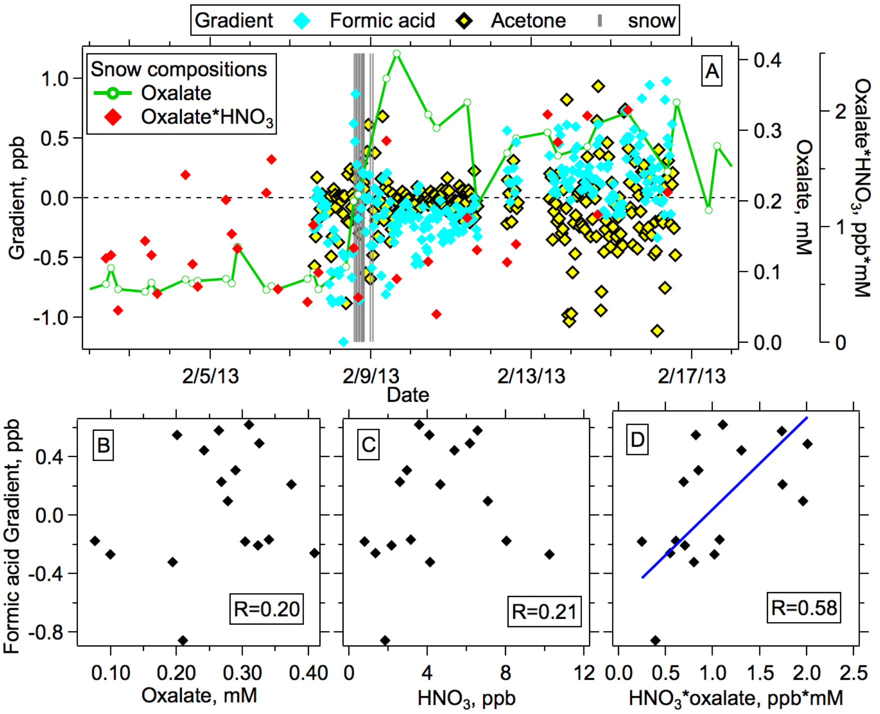

Fig. 2 (A) Time series of concentration gradients of formic acid and acetone during UBWOS 2013. Time series of oxalate measured in melted snow water and the product of oxalate in the snow and nitric acid ($HNO_3$) in ambient air are also shown. The vertical black bars indicate periods with snow fall. (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).

# References:

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