Author Response to Reviewer 1 – Modeling the Diurnal Variability of Agricultural Ammonia in Bakersfield, California during the CalNex Campaign

We would like to sincerely thank both reviewers and the editor for their time and contribution to reviewing this paper. We have responded below, with reviewer comments in bold, and author response in italics.

Suggestions for revision from Reviewer 1:
The recent revision has greatly improved the manuscript, and in my opinion could be improved to be ready for publication after a final set of revisions. The requested revisions mostly cover the results & discussion as to my opinion some conclusions are made to lightly and/or are not completely supported by the results the authors show. A few comments/edits are minor details and will only take a few minutes to correct. A few others are more in depth and touch the basis of the manuscript. The authors do not need to completely agree to all statements but some elaboration will be needed to convince me and to my expectation most of the readers.

In depth comments/discussion:
Overall & page 11 line 12-20 about the scaling factor of the emissions; You describe that you directly scale emissions needed to match a ratio of measured to modelled concentrations. What you more or less assume in this case is that the ammonia emissions is linearly related to ammonia concentration.

Can you shortly discuss the scientific basis behind this assumption, and why not use a somewhat lower or constant factor?

Our reasoning for choosing the diurnal scaling emission was due to the fact that the modeled to measured ratio of NH₃ at the Bakersfield site suggested that the largest error was due to a missing factor with a diurnal pattern. While the CARB inventory did not include diurnally-varying NH₃ emissions, other emission inventories have included such a distribution (Zhu et al. 2015a, Bash et al. 2015), so we chose to hypothesize this as a solution. The total emissions for the day were kept as the original CARB emission inventory suggested, for each grid box of the model. We agree that lower or constant factors may also be representative, but were not explored in this paper, as our main goal was to address the apparent diurnal error from the surface measurements and how it affected model comparisons with the TES instrument; additional model simulations were beyond the scope of the project.

Our assumption of a linear relationship between ammonia emissions and ammonia concentrations was based on mass balance considerations. If wind speed, deposition, and PBL height are held constant a simple box model over the Bakersfield site would show a linear relationship between additional NH₃ emissions and the NH₃ concentration, since there is not enough sulfate to react with all the NH₃ (Seinfeld and Pandis, 2006). However, we believe that errors in other parameters (PBL height, deposition, etc.) affect modeled NH₃ and NH₄ concentrations more strongly, and so we focused on these parameters in the rest of the paper. We added language describing the expected reaction of NHs in an ammonia rich region, Page 11 Lines 33-35 to Page 12 Lines 1-5:

"The intense agricultural activities in the SJV generate large NH₃ emissions, with concentrations often exceeding 5 ppb as indicated in the ground measurements, making this an NH₃ rich region relative to the ambient sulfate concentrations. In this regime, since there is not enough sulfate to react with all the NH₃, a simple box model over the Bakersfield site, with wind speed, deposition, and PBL height variation held constant, would show a linear relationship between additional NH₃ emissions and the NH₃ concentration (Seinfeld and Pandis, 2006). Thus we expect errors in other parameters (PBL height, deposition, etc.) to
Page 10, line 10-14, you mention the effect of hourly varying emissions, and that the diurnal variation is missing.

Emissions in the CARB inventory do vary month to month. However, in order to study the monthly variation of emissions, we would need a much longer time period of data, as the CalNex campaign only ran from May to June of 2010. Thus this paper can only discuss varying emissions for that time frame. The summer time frame also allowed us to make the assumption that particulate formation played a minor role in the resulting NH$_3(g)$ concentrations, already discussed on the paper on Page 2 Lines 23-24. We have also added the following to Page 9 Lines 8-9:

“While emissions do vary month-to-month, we do not explore seasonal variation in this study, since the measurement campaign only occurred during the months of May and June.”

Overall & discussion of effects of transport; I do not fully agree with the explanation / conclusion that transport of ammonia does not seem to be a major factor. Although you cover the basis of wind direction there is a short discussion missing on the effects of wind speed. Towards the north-west the ratio between livestock/fertilizer applications is probably different compared to the local conditions at Bakersfield, CA. As my personal knowledge of the counties surrounding Bakersfield is non-existing I cannot couple the summary of the sources given in S2 to the concentrations measured at the Bakersfield site (when combining this to the wind speeds, and assuming a more or less constant wind direction. Would it be possible to add a figure in which you compare windplots of the model (a) with measured concentrations (b). Radially you can show the measured concentrations, coloring can show the wind speed (or vice versa). This will support the explanation that transport / horizontal misrepresentation of the emissions are not a major cause of the difference between model and measured concentrations.

To somewhat support my statement; you show that the model underestimates the RVMR to the north west compared to the satellite, while locally its basically the same, wind speeds increase to the end of the day compared to the overpass time of TES (13:30). Even if you would perfectly model the local emissions in the Bakersfield model cells, the misrepresentation to the north-west could possibly cause of bias shown in figure 3 & 9.

We have performed an extensive investigation in response to the reviewer’s suggestion of looking into measured and modeled wind speed and direction versus NH$_3$ concentrations. Below are two plots showing the measured wind direction versus measured NH$_3$ (left) and CMAQ wind direction versus CMAQ NH$_3$ concentration (right) measured at the Bakersfield site that is now Figure 3 in the paper. We also include an additional Figure S5 in the supplement comparing modeled and measured wind speed.
Figure 3. Wind rose of measured wind direction and NH₃ on the left, and modeled wind direction and NH₃ on the right where contours represent number of data points (hourly) per wind direction. Note the difference in scale, where values are in ppb.
In two locations in the paper we describe results from these figures on Page 11 Lines 2-18:

“During the nighttime there is a shift in wind direction to sources coming from the southeast. Cooling air from up in the eastern mountain ranges causes a mountain drainage effect into the southern valley area. This interaction of the mountain drainage combined with the typical low-level jet from the northern central valley creates a Fresno Eddy, as described in Michelson and Bao (2008). Figure 3 shows a wind rose for all points included in Figure 2, where measured wind direction and NH₃ concentrations are shown on the left, and modeled wind direction and NH₃ concentrations are shown on the right. It can be seen in Figure S5a that the nighttime wind measurements from the southeast generally have lower wind speeds (≤ 4 m s⁻¹) and that the model does not capture the variation of these wind speeds very well. This may be due to some timing errors in that the model may not capture true winds within a 4 km grid box, which corresponds to about 1-2 hours in real time. In general, many of the higher modeled NH₃ concentrations appear to be occurring during nighttime when the model should have winds out of the southeast, thus there is large model bias for these points. As indicated by the performed HYSPLIT back-trajectories, and the description
of air flow in the southern valley, we assume that although the measurements indicate the immediate wind
direction was out of the south-east, the air-mass’s long-range transport still travelled over the Central
Valley to accumulate emissions from that region before being recirculated by the Fresno Eddy to
eventually come from the southeast. Thus, an overestimate of emissions in the Central Valley at night could
still contribute to a model overestimate of measurements coming out of the southeast, rather than this air
mass having come from a cleaner source, east of the mountains. Additionally, for the remaining time
periods and majority of measurements not out of the southeast at nighttime, the model does a better job at
simulating wind speeds (Figure S3), with a large model bias in NH\textsubscript{3} concentrations remaining."

And additionally on Page 12 Lines 30-34:

"Furthermore, when we compare the modeled NH\textsubscript{3} to measured values coming from just the southeast at
night (Figure S5), the model bias is reduced by about factor of 3.5. This suggests that although the model
may not capture the immediate wind direction and wind speed at night, as explained above, because of the
long-range transport down the Central Valley that evolves into the Fresno Eddy, reducing emissions in this
upwind region also reduces model bias for these points in time."

This is also supported by the HYSPLIT back trajectories we have run (Figure S2) and further demonstrated in the fact that
when we do apply the diurnal emissions profile, we see a reduced model bias in all wind directions, with a larger reduction
in bias when the winds are out of the southeast (Figure S5c). Thus, even with the apparent errors in the modeled wind
direction and speed at Bakersfield, the magnitude of emissions, assuming the linear response of concentrations to emissions
in this NH\textsubscript{3} rich regime (> 5ppb), is too high during this time of day from upwind sources, which in this case we assume to
be the Central Valley.

Table S2; Add some coordinates or relative position compared to Bakersfield. Or a small map showing the counties?

The position of Bakersfield, California is shown in Figure 1 as the red star, on the colored background of emissions, with the
highest emissions located in the Central Valley. We have also added county lines to Figure 1 and feel this is sufficient to
familiarize the reader with how emissions are distributed with respect to the ground site and the flight and satellite tracks.

Also what does Farming Operation mean? And what about livestock? Is this part of Farming Operation?

In the CARB emissions inventory there are 3 categories of NH\textsubscript{3} emissions, which includes 1) emissions from
pesticide/fertilizer application, 2) farming operations, which in this inventory includes livestock agriculture in all forms
including handling of all excrement and 3) other NH\textsubscript{3} emissions that do not fall into either of the previous categories. This is
already described in the paper on Page 12, Line 14-18.

Overall discussion of the statistics in Table 1 & 2; What I am missing is an in depth discussion of the statistics given
in Table 1 and 2. What essentially is shown in Table 1 is that there is zero correlation between the model and the
measurements, i.e. any statements made on the bias will not convince anyone and I think it does not fully reflect the
performance of the CMAQ model as even using CMAQab only gives a correlation of 0.05. A few lines on why these
correlations are so low will improve the manuscript and re-establish faith in the CMAQ models capabilities to
simulate NH\textsubscript{3}.  

| 5 |
Table 2 & Section 4.2: At a first glance I would conclude that CMAQ base is better than CMAQab or CMAQb. Even though the diurnal variation is improved for the hours between 1 AM and 6 AM, the overall levels for the other 3/4 of the day are still too high or too low depending on the hour. Only a short discussion is given of CMAQB and CMAQab, page 12, line 24-31. You correctly point out that the emissions are now far too high for most of the day for both “improvements”. The same is visible in Table 1 and somewhat less in table 3 as TES only gives a snapshot of the situation at 13:00.

We thank the reviewer for the comments regarding the statistics of the paper. We have chosen in the paper to mostly discuss model errors in terms of the mean bias and normalized mean bias, and to focus on those errors that can be addressed by adjusting the diurnal cycle of NH₃ emissions, as has been done for other inventories (e.g., Bash et al. 2015). We did this as the analysis of the Bakersfield surface observations showed a large diurnally-varying model error, which would be expected to significantly affect comparisons with datasets that did not cover the entire day, such as the satellite and aircraft observations. We believe that these errors needed to be addressed first before any further investigation into errors in the magnitude of the total emissions, day-to-day variation in emissions (possibly accounting for the poor observed correlation), or the vertical transport of NH₃ (possibly affecting the aircraft observations). While we plan to address these other errors in future work, we feel that our investigation into the possible sources of the diurnal errors is sufficiently complex that it needs to be summarized in its own manuscript.

However, we agree with the reviewer, especially in the ground and flight measurement discussion, that the small correlations ($r^2 < 0.1$) should be pointed out to the reader, thus we have done so by highlighting low $r^2$ values (less than 0.1) in italics, removed any wording suggesting we have made any ‘improvements’ to these correlations and, when possible, emphasized the low correlations to the reader. For example on Page 13 Lines 1-2 we have added:

“However, we note that the correlation of all three-model scenarios remains very low ($r^2 < 0.06$), suggesting further model errors, such as the neglect of any day-to-day variation in NH₃ emissions in our simulations.”

We feel, however, that since the original model runs (CMAQbase) also have low correlations for these measurements, that the investigation of possible diurnal errors in ammonia surface fluxes is justified, and that this investigation and manuscript is useful to readers.

This brings me to a point to question the value of CMAQb and CMAQab to the manuscript. While the authors do a good job describing the possible causes of error in the base model, the new additions do not improve the model and are thus somewhat irrelevant in the current state besides showing that it is not correct to scale emissions following concentrations and that the current bi-directional schemes are far from perfect, things that have been shown before. I would like to put forward two possible approaches to make the manuscript ready for publication.

1. Change the manuscript to fully focus on the performance of CMAQbase & CMAQb. These two versions of the model have been described before in earlier publications and only a small addition to the result section, to better cover the CMAQb results, will be needed to improve the manuscript enough for publication. Especially as possible causes of CMAQb are already mentioned in the discussion.

2. If the authors want to keep in the CMAQb model more work will be needed. Rethink the scaling of the emissions, improve the description of the scientific basis behind the scaling as it is currently somewhat lacking. Furthermore make the improved CMAQab version the focus of the manuscript. In the current state it is mentioned in only a few sentences, raising the question why it is included in the first place, except to somewhat improve the diurnal variation, at which CMAQab is currently doing a poor job.
We thank the reviewer for their very thoughtful and thorough discussion and suggestions. We have decided to follow approach 2 provided by the reviewer. In order to justify why the CMAQab modeled scenario was performed, we refer the reviewer to the new description of our assumption of the linear relationship of emissions to concentrations, as well as the more thorough discussion on wind transport in the Bakersfield area, discussed in the above comment responses. We have also added discussion to Section 4.2 and 4.3 to focus more on the CMAQab modeling results in addition to adding CMAQab results to the new Figure 4, which allows for easier comparison to the original CMAQbase run. Figure 6 now includes a flight comparison using CMAQab results, instead of CMAQb, to enhance the discussion in Section 4.2 of aircraft comparisons, and vertically modeled NHx. Finally, we have also included CMAQab results of CMAQ modeled RVMR in Figure 8, comparing to TES RVMR, to allow a more in-depth and visual comparison of how the CMAQab model performs. We feel that with these additions to the plots, discussion, and organization of sections that the paper is significantly improved, with thanks to the reviewer.

**Minor Edits:**

Table 1: Add a description of MB and MNB, also add this to the text. Add the number of observations?

We thank the reviewer for suggesting this description. We have added a description to the header of Table 1, and point the reader to this description in the text (Page 10, Line 10), and in Tables 2 and 3. The text reads: Mean Bias (MB) = mean modelled – measured, Mean Normalized Bias (MNB) = mean ((modelled – measured)/measured)

Discussion of Table 1: you show correlations of around 0.001 to 0.05. At this point statistics about slopes and MB become more or less irrelevant as you are applying fits to clouds of scatter. Maybe some explanation as to why the correlations are so low, at least mention it in the text. Correlations are almost not mentioned in the text, unless they are high ~0.7…, don’t hide the fact that the model misrepresents the measured values even after the CMAQab additions.

Table 2; similarly to table 1, add a description of MB and MNB. Add the number of observations?

Table 3; add description of MB and MNB. Add the number of observations?

We have added discussion throughout the paper to emphasize the small correlations. For example, on Page 12 Line 8-10:

“However there is still a clear model NHx overestimate overall (MB of 4.37 ppb and large MNB of 45.74 %, see Table 1), and the low correlation is not improved (r² = 0.01).”

Figure 1; Colorbar label: Add an E to emission. Also change font to the same font of the colorbar ticks?

We thank the reviewer for pointing out the typo and have corrected this and the font.

Figure 2; If possible add Wind Direction, My explanation is added in the in depth comments.

We respond to the suggestion of wind direction in the comments above. We have added wind direction to Figure 4 (green line in bottom panel) as well as the addition of a windrose plot in the new Figure 3.

Figure 3; If possible make one big figure with 4 subplots using figure 3a b and 9 a b. This will make it easier for the reader to compare the old and new situations, Also add the Blue “observed” plot to 9b.
We strongly agree with the reviewer’s comment here, and feel as though this new figure would create much easier comparisons, thus we have updated Figure 3 (which is now Figure 2) to include the additional plots of old Figure 9, and changed the text to reflect this, also included below (Page 15, Lines 10-19):

‘Model bias in both the night and daytime simulation of surface NH$_x$ is reduced in the CMAQ$_{ab}$ scenario. The total bias is significantly reduced from the factor 4.5 at night and 0.6 during the day compared to the CMAQ$_{base}$ scenario (Figure 4a). In CMAQ$_{ab}$ the model does well between the hours of 1:00 am and 6:00 am local time (Figure 4c), perhaps related to the lower emissions at this time of day when adjusted emissions are used assuming the linear relationship of emissions to concentrations. The remaining diurnal bias shows a relative model underestimate with a factor of $\sim$0.6 at 10:00 local time and a relative model overestimate peaking at $\sim$1.7 at 19:00 local time (Figure 4c), with average CMAQ$_{ab}$ modeled concentrations slightly higher in the afternoon and peaking around 19:00 (Figure 4d). It is interesting to note that the CMAQ$_{ab}$ bias relative to surface concentrations is small near the TES overpass time (e.g., crossing 0% between 13:00 and 14:00 local time, Figure 4c), which is consistent with the small bias seen in the comparison with the TES observations in Section 4.3.”

Figure 4, Good figure, as for colors, maybe blue and red? Easier to distinguish the differences.

We recognize the reviewers comment, however feel as though changing the colors to red and blue may confuse it with the CMAQ model and measurement comparisons, thus we would like to keep these colors so as to make this a clear distinction.

Figure 5, Maybe also add 2010/06/16 CMAQ B for the top figure? Else remove the top subplot. What about CMAQ AB? Another possibility: Change it to 2 figures, one for 2010/06/16 and one for 2016/05/24 both with 3 subplots, CMAQ base, B and AB. Also show the figures in chronological order.

We recognize the reviewer’s comments here, and have chosen to replace the CMAQ$_{B}$ (bottom panel) with a CMAQ$_{AB}$ comparison. We keep the same three panels otherwise to show the daytime ability of CMAQ$_{base}$ to capture ’hot spots’ of ammonia (first panel), the nighttime ability of CMAQ$_{base}$, which seems to contain NH$_x$ in the bottom layer of the model (second panel), and finally the third panel, which shows the increase in vertically modeled ammonia in the CMAQ$_{ab}$ model. We feel that excluding any of these panels would be taking away from the in-depth comparison in the paper. We not that Table 2 still describes the relevant statistics for all other flights, with the low $r^2$ values (less than 0.40), are italicized to point out to the reader.

Figure 7, Add in CMAQ B, CMAQ AB for comparison.

We have added both CMAQ$_{ab}$ and CMAQ$_{AB}$ to Figure 7 (now Figure 8) to compare to the CMAQ$_{base}$ run, shown below. The statistics of this figure remain in Table 3.
Page 7, line 28; W is a weighting matrix, add a few words on how the matrix is calculated (possible effects following such a mapping).

We have clarified the description of the CMAQ representative volume mixing ratio (CMAQ_RVMR) to also include a description of the weighting matrix calculation as follows (Page 7, LN 24-30):

\[
x_{\text{TES}} = x_a + A(x_{\text{CMAQ}} - x_a)
\]

and the RVMR is calculated as

\[
\text{CMAQ}_{\text{RVMR}} = W \cdot x_{\text{TES}}
\]

where \(x_a\) is a vector of the TES a priori \(\text{NH}_3\) concentrations, \(A\) is the averaging kernel matrix, \(x_{\text{CMAQ}}\) is a vector of the interpolated CMAQ \(\text{NH}_3\) values, and \(W\) is a weighting vector (Rodgers and Connor, 2003; Shephard et al., 2011). \(W\) basically weights each level according to the sensitivity of the TES instrument at
that level. It is calculated by summing the most significant rows of the averaging kernel at each level (see the appendix in Shephard et al., 2011 for details).

References added to text:

Author Response to Reviewer 2

Page 8, line 9. Define “RRTMG”.”

Page 8, line 6-8. Could you indicate the reasons why you need to use initial and horizontal boundary conditions from another model?

The WRF-ARW model is a limited-area model, thus requiring independent boundary-conditions data from a larger scale model. Additionally all Eulerian models require initialization input for the execution of simulations. For consistency, both the boundary and initial conditions are taken from the same model.

Page 11, line 23-24. I guess you mean “CMAQ_base” and “CMAQ_B”

Yes, we thank the reviewer for pointing this out and have made this correction.

Page 13, line 5. I don’t think this conclusion can be made based on the figure. The locations of different sources of NH3 are still not clear to me based on the figure.

The wording has been changed in an effort to be more clear. It now reads on Page 14, Lines 10-13,

“Applying the TES operator to the CMAQ profiles and calculating the CMAQ_RVMR allows us to compare the satellite and model datasets quantitatively, as described in Section 2.3. Surface NH3 from the CMAQ_base run (Figure 7a) and the TES NH3 RVMR (Figure 7b) along a sample TES transect both identify the regions of large NH3 sources and the spatial changes along the transect and demonstrate that the CMAQ_RVMR is underestimated for the base run, particularly at higher NH3 RVMRs.”

Page 13, line 9. The r2 of 0.64 is not a well-correlated case to me. I don’t think “CMAQ_base inventory does a good job of capturing the spatial distribution of NH3 emissions near Bakersfield” based on the r2 of 0.64 and mean bias of -2.67 ppbv. I suggest the authors either soften the words or remove this conclusion.
We have removed the strong words indicating the correlation is “good” however we feel as though the model can still qualitatively capture the regions of higher NH₃ emissions, as with the TES instrument. Thus we have changed the wording on Page 14, Lines 10-22, that describe the model evaluations with TES measurements.

‘Applying the TES operator to the CMAQ profiles and calculating the CMAQ_RVMR allows us to compare the satellite and model datasets quantitatively, as described in Section 2.3. Surface NH₃ from the CMAQ_base run (Figure 7a) and the TES NH₃ RVMR (Figure 7b) along a sample TES transect both identify the regions of large NH₃ sources and the spatial changes along the transect and demonstrate that the CMAQ_RVMR is underestimated for the base run, particularly at higher NH₃ RVMRs. Similar results were found for other transects and summarized in Table 3 and Table S2. The time of the satellite overpass occurs just prior to the peak of emissions in the emission factor applied to the CMAQ_AB case which in turn increases the RVMR bias to 1.31 ppbv and increases the regression slope to 1.02 (purple line Figure 8) as compared to a bias of -2.57 and slope of 0.40 in the CMAQ_base case. The slope of the linear regression of CMAQ_AB RVMR suggests that CMAQ run with bi-directional ammonia along with the applied emissions factor slightly overestimates NH₃ concentrations, indicating the magnitude of the emissions factor may be too high at the time of satellite over pass. The inclusion of the emission factor in this CMAQ_AB case has a higher bias than the bi-directional model run, CMAQ_B. This demonstrates the importance of using highly time-resolved observations of NH₃ to determine the diurnal cycle of NH₃ along with polar-orbiting satellite retrievals of NH₃ to improve the spatial and seasonal distribution of the emissions, as noted in Zhu et al. (2013).’

Figure 3. I suggest changing y label to “Ratio”.

We agree with the reviewer, and have replaced the y label with ‘Ratio’, while defining the distinction between NH₃ and NHₓ in the legend.
Modeling the Diurnal Variability of Agricultural Ammonia in Bakersfield, California during the CalNex Campaign


Abstract. NH$_3$ retrievals from the NASA Tropospheric Emission Spectrometer (TES), as well as surface and aircraft observations of NH$_3$ and submicron NH$_4$ can be used to evaluate modeled concentrations of NH$_3$ and NH$_4$ from the Community Multiscale Air Quality (CMAQ) model in the San Joaquin Valley (SJV) during the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign. We find that simulations of NH$_3$ driven with the California Air Resources Board (CARB) emission inventory are qualitatively and spatially consistent with TES satellite observations, with a correlation coefficient ($r^2$) of 0.64. However, the surface observations at Bakersfield indicate a diurnal cycle in the model bias, with CMAQ overestimating surface NH$_3$ at night and underestimating it during the day. The surface, satellite, and aircraft observations all suggest that daytime NH$_3$ emissions in the CARB inventory are underestimated by at least a factor of two, while the nighttime overestimate of NH$_3$ is likely due to a combination of overestimated NH$_3$ emissions and underestimated deposition.

Running CMAQ v5.0.2 with the bi-directional NH$_3$ scheme reduces NH$_3$ concentrations at night and increases them during the day. This reduces the model bias when compared to the surface and satellite observations, but the increased concentrations aloft significantly increase the bias relative to the aircraft observations. We attempt to further reduce model bias by using the surface observations at Bakersfield to derive an empirical diurnal cycle of NH$_3$ emissions in the SJV, in which nighttime and midday emissions differ by about a factor of 4.5. Running CMAQv5.0.2 with a bi-directional NH$_3$ scheme together with this emissions diurnal profile further reduces model bias relative to the surface observations.

Comparison of these simulations with the vertical profile retrieved by TES shows little bias except for the lowest retrieved
level, but the model bias relative to flight data aloft increases slightly. Our results indicate that both diurnally-varying emissions and a bi-directional NH$_3$ scheme should be applied when modeling NH$_{3,0}$ and NH$_{3,1}$ in this region. The remaining model errors suggest that the bi-directional NH$_3$ scheme in CMAQ v5.0.2 needs further improvements to shift the peak NH$_3$ land-atmosphere flux to earlier in the day. We recommend that future work include: updates to the current CARB NH$_3$ inventory to account for NH$_3$ from fertilizer application, livestock, and other farming practices separately; adding revised information on crop management practices specific to the SJV region to the bi-directional NH$_3$ scheme; and top-down studies focused on determining the diurnally-varying biases in the canopy compensation point that determines the net land-atmosphere NH$_3$ fluxes.

1 Introduction

The emissions of ammonia (NH$_3$) to the atmosphere are highly uncertain (e.g., Pinder et al., 2006; Beusen et al., 2008; Galloway et al., 2008; Henze et al., 2009; Schlesinger, 2009). Nitrogen dioxide (NO$_x = NO + NO_2$) and sulfur dioxide (SO$_2$) photo-oxidize in the atmosphere to form nitric acid (HNO$_3$) and sulfuric acid (H$_2$SO$_4$), respectively, which react with atmospheric gas-phase ammonia (NH$_3$) to form ammonium sulfate ((NH$_4$)$_2$SO$_4$) and ammonium nitrate (NH$_4$NO$_3$) aerosols. Uncertainty in NH$_3$ emissions therefore leads to significant uncertainties in the concentrations of secondary inorganic aerosols. Ammonium sulfate and nitrate aerosols contribute to fine particulate matter concentrations (PM$_{2.5}$), and thus to decreased visibility, altered climate, and acidification and eutrophication in sensitive ecosystems (e.g., Paulot et al., 2014; RoTAP, 2012; Bricker et al., 2007; Martin et al., 2004). PM$_{2.5}$ also causes adverse health effects (WHO, 2016; Pope et al., 2004). In particular, some regions in the San Joaquin Valley (SJV) in California have been designated as non-attainment areas for PM$_{2.5}$, with NH$_3$ emissions contributing to more than half of the inorganic PM$_{2.5}$ in the state (Schiferl et al., 2014), depending on ambient conditions and concentrations (Lonsdale et al., 2012). During the NOAA California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign in May and June of 2010, however, concentrations of PM$_{2.5}$ rarely exceeded the National Ambient Air Quality Standard (NAAQS) in the SJV, as PM$_{2.5}$ exceedances here generally occur in the winter. While emissions of NO$_x$ and SO$_2$ are relatively well constrained, are regulated by the United States Environmental Protection Agency (US EPA), and are predicted to continually decrease due to air quality regulations and emission reducing technologies (US EPA, 2010), NH$_3$ emissions are not currently regulated and are predicted to stay constant or increase in the US over the next several decades in the US due to an increasing population and associated increases in farming and agricultural activities (Moss et al., 2010). Climate change is also predicted to increase NH$_3$ emissions (+0-40 % in north-central Europe) with larger countries having the largest uncertainty in emissions variations (Skjøth et al., 2013).

Anthropogenic NH$_3$ sources in the SJV are dominated by agricultural activities, with livestock waste estimated to contribute about 74 % of total anthropogenic NH$_3$ to the atmosphere and chemical fertilizer use another 16 % (Simon et al., 2008). Agricultural emissions of NH$_3$ can be highly variable due to factors such as the differences in fertilizer application, the diet...
provided to livestock, and waste management and storage practices of farmers (Hristov et al., 2011; Sawycky et al., 2014). In addition, while NH$_3$ can be quickly deposited to the surface causing soil acidification, water eutrophication, and an imbalance of ecosystems when in excess (e.g., Carfrae et al., 2004), the air-surface exchange of NH$_3$ is bi-directional, with the direction of the NH$_3$ flux between the land and the atmosphere varying with temperature, relative humidity, vegetation and soil type, maintenance (e.g., cutting and tilling practices), and fertilizer applications (Nemitz et al., 2001; Zhang et al., 2010; Ellis et al., 2011; Bash et al., 2013; Sawycky et al., 2014). This complexity in the emission and deposition of NH$_3$, along with the rapid reactions of NH$_3$ with HNO$_3$ and H$_2$SO$_4$ and the consequently short (~1 day) atmospheric lifetime of NH$_3$, leads to large temporal and spatial variability as seen in in situ measurements (e.g., Langford et al., 1992; Carmichael et al., 2003; Nowak et al., 2010; Walker et al., 2013) and in satellite retrievals (e.g., Clarisse et al., 2013; Pinder et al., 2011; Shephard et al., 2011; Heald et al., 2012; Sun et al., 2015; Shephard and Cady-Pereira, 2015; Shephard et al., 2015).

Recent studies have recognized a diurnal pattern in NH$_3$ emissions from livestock attributed to potential differences in farm management practices, livestock housing outflow patterns, and variations in soil moisture, temperature, and wind speed (Hensen et al., 2009; Zhu et al., 2015a; Zhu et al., 2015b). To account for this, a diurnal variability scheme was implemented into global simulations using the global 3-dimensional chemical transport model, GEOS-Chem, and was shown to decrease NH$_3$ concentrations globally (Zhu et al., 2015a). That study also calculated the bi-directional exchange of NH$_3$, which decreased NH$_3$ concentrations in the US in the months of October through April and increased it in the month of July (Zhu et al., 2015a). Bash et al. (2013) also explored the sensitivity of modeled NH$_3$ concentrations to a bi-directional NH$_3$ scheme that used meteorological factors, including temperature, wind speed, agricultural crop flux values, and a nitrogen soil geochemistry parameterization in the CMAQ model. They found that over the continental US their model run with the bi-directional NH$_3$ scheme decreased the total dry deposition of NH$_3$ by 45 %, thus increasing atmospheric NH$_3$ concentrations and NH$_4^+$ wet deposition by 10 % and 14 %, respectively. Wichink Kruit et al. (2012) use the DEPosition of Acidifying Compounds (DEPAC) surface-atmospheric exchange module in a CTM and saw an increase in atmospheric NH$_3$ almost everywhere in their model domain, including decreased NH$_3$ deposition with a remaining underestimation in agricultural areas.

Previous studies have also shown that errors in NH$_3$ emissions are a common contributing factor to modeled PM$_{2.5}$ and NH$_3$ bias (e.g., Schiferl et al., 2014). Skjøth et al., (2011) discuss their method for calculating dynamic NH$_3$ emissions that includes distributions of agricultural NH$_3$ in Europe. Their method is designed for use in chemical transport models and their results show considerable improvements made in the agricultural NH$_3$ sector, particularly in areas with detailed records of agricultural practices. Inverse modeling studies have been used to reduce the uncertainty in NH$_3$ emissions as well, generally by assimilating surface observations of the wet deposition of ammonium (NH$_4^+$) in precipitation. Gilliland et al. (2003) used the CMAQ model to determine that the 1990 version of the US EPA National Emissions Inventory (NEI) overestimated total emissions of NH$_3$ by 20 %. Gilliland et al. (2006) performed a similar study for the 2001 NEI and found that total emissions of NH$_3$ were represented well, but needed to be increased in summer and reduced in winter. Henze et al. (2009) used the
adjoint of the global chemical transport model GEOS-Chem to assimilate the Inter Agency Monitoring of Protected Visual Environments (IMPROVE) observations and found that total US NH$_3$ emissions for 1998 were overestimated. More recently, satellite observations of NH$_3$ have been incorporated into inverse studies. By assimilating satellite retrievals of NH$_3$ concentrations from the Tropospheric Emission Spectrometer (TES) (Beer et al., 2008; Shephard et al., 2011) aboard the NASA Aura satellite, it has been found that NH$_3$ emission sources in GEOS-Chem are broadly underestimated (Zhu et al., 2013). Heald et al. (2012) and Walker et al. (2012) used IMPROVE data and satellite retrievals of NH$_3$ from the Infrared Atmospheric Sounding Instrument (IASI, Van Damme et al., 2014) to show that NH$_3$ emissions are likely underestimated in GEOS-Chem for California, leading to a local underestimate of NH$_3$(a). Other infrared nadir sounders have been used to provide satellite observations of NH$_3$. For example, Shephard and Cady-Pereira (2015) demonstrated the ability of the Crosstrack Infrared Sounder (CrIS) aboard the joint NOAA-NASA Suomi National Polar-orbiting satellite to measure daily, spatially distributed tropospheric NH$_3$ in California, and in preliminary results found it correlated well with Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) aircraft measurements in the SJV in January 2013.

Investigating the formation, transport, and fate of NH$_3$(a) and NH$_3$(g) in California was one of the major goals of the CalNex field campaign, which provided measurements from flights and surface sites (Ryerson et al., 2012) in the Los Angeles basin and in the Central Valley. Nowak et al. (2012) used these data to demonstrate the importance of ammonium nitrate formation downwind of the Los Angeles urban core and dairy facilities further east. They found that NH$_3$ emissions from these dairy farms were underestimated by a factor of 3 or more, thus indicating the need for better representation in this emission sector. Kelly et al. (2014) in general saw well-correlated comparisons of CMAQ model estimates to measurements from the EPA’s Chemical Speciation Network. Their model tended to under-predict NH$_3$ (NH$_3$ = NH$_3$(g) + NH$_3$(a)) during the day at the Bakersfield, CA site and significantly over-predict NH$_3$(a) at night. They suggest that this model bias may be due to emissions from livestock and dairy farms being too low and lacking in variability in this region or to errors in crustal cation predictions and the missing effects of organic acids and amines on inorganic aerosol thermodynamics (Kelly et al., 2014).

Model estimates of the planetary boundary layer (PBL) height are essential in correctly quantifying changes in atmospheric pollutant concentrations, especially for short-lived pollutants like NH$_3$. Such estimates are difficult at fine spatial and temporal scales, especially in the complex terrain of the SJV. Scarino et al. (2014) studied the PBL and mixed layer heights during CalNex using WRF and high spectral resolution lidar (HSRL) data taken during the campaign. They found that, in general, there is good agreement between the WRF modeled output and measured values; however, in the California Central Valley there is a WRF mixed-layer height over-prediction and an inability to represent the diurnal growth of the mixed layer in the early part of the day. Additionally they suggest that future improvements will require a focus on mixing layer characteristics, soil moisture, and temperature. Baker et al. (2013) explored how well the WRF model configuration used to drive the CMAQ simulations of Kelly et al. (2014) simulates PBL height during CalNex, using two versions of WRF. The study shows that both WRF versions simulate the PBL and mixing layers well within the SJV, as well as other large scale flow patterns, but under-predict local wind speed and temperature. A strong aerosol gradient is used to identify the top of the
PBL in HSRL measurements; this strong gradient may also be present in a nighttime residual layer. Baker et al. (2013) take this into account by identifying the surface-attached mixed layer, which they assume as the lowest significant gradient in such a circumstance.

In this study, we use the CalNex observations of NH$_3$(g) and NH$_4$(p) and the CMAQ model to evaluate the estimates of NH$_3$ emissions in the SJV contained in the California Air Resources Board (CARB) inventory (Figure 1). While previous NH$_3$ model evaluation efforts using CalNex data have focused on the NEI inventory (Kelly et al., 2014; Heald et al., 2012; Walker et al., 2012), the CARB inventory is used in the development of California’s State Implementation Plans (SIPs) under the Clean Air Act, and so ensuring the accuracy of this emission inventory is important to the design of air quality policy for the SJV and California in general. In addition, previous studies have not taken advantage of the high-resolution observations of NH$_3$(g) made by the TES satellite instrument over Bakersfield during the CalNex campaign. Here we evaluate the consistency of the satellite, aircraft, and surface observations of NH$_3$(g) and NH$_4$(p) during the CalNex campaign and then use these observations, along with lidar retrievals of PBL height, to investigate the biases in the magnitude and diurnal cycle of emissions of NH$_3$(g) from the CARB inventory in the SJV. We also explore the sensitivity of modeled NH$_3$ concentrations to bi-directional NH$_3$ exchange using the bi-directional NH$_3$ flux scheme in CMAQv5.0.2.

Section 2 briefly describes the data sources used in this study, while Section 3 describes the CARB emission inventory and the configurations used for the WRF, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT), and CMAQ model runs. The performance of the CARB inventory used in our CMAQ simulations, along with model sensitivity studies, is presented in Section 4. Section 5 discusses the remaining errors in our final model configuration in detail and makes suggestions for further model improvements, while our conclusions are discussed in Section 6.

2 Data

2.1 NOAA WP-3 aircraft

The NOAA WP-3 aircraft completed 18 research flights during the CalNex campaign, which included measurements of NH$_3$(g) and NH$_4$(p). NH$_3$(g) was measured at 1 s (~100 m) intervals using chemical ionization mass spectrometry (CIMS) with an uncertainty of +/- 30% as described in detail in Nowak et al. (2007). The CIMS instrument sampled air through a 0.55 m long heated teflon inlet with a fast flow. Measurement artifacts were accounted for by quantifying and subtracting the background signal originating from NH$_3$ desorption from instrument surfaces. The background signal was determined in flight by actuating a teflon valve at the inlet tip once every half hour to divert the sample air through a scrubber that removes NH$_3$ from the ambient air stream (Nowak et al., 2007). Additionally, standard addition calibrations from a NH$_3$ permeation tube were performed several times each flight to determine instrument sensitivity. Submicron NH$_4$(p) was measured at 10 s (~1 km) intervals with an uncertainty of ~ 30% using a compact time-of-flight aerosol mass spectrometer from Aerodyne (c-TOF AMS, Bahreini et al., 2009). In this study we focused on the flights of 24 of May and 16 and 18 of June when the WP-3 was sampling air in the SJV (Figure 1). The quality-controlled flight data were reported at a merged time resolution of 1 s,
which we averaged to 1 minute values (the approximate time it takes the WP-3 to cross a 4 km CMAQ grid box) and then matched the sample times and locations to the corresponding time and location of the CMAQ hourly concentration output.

2.2 Bakersfield surface observations

Bakersfield, California is located in the southern part of the SJV (35.35°N, 118.97°W, 20 m asl) and there is a general north-to-south orographic air-flow in this region, with a tendency for emissions to get trapped in the valley due to the nearby mountains (Baker et al., 2013). At the Bakersfield ground site the Ambient Ion Monitor Ion Chromatograph (AIM-IC; Ellis et al., 2010, Markovic et al., 2012) was used to measure NH$_3$$_3$ on an hourly basis, with an uncertainty of ±20% and a detection limit of 41 ppt. The sampling inlet for the AIM-IC consists of an enclosure mounted at 4.5 m above ground, including a virtual impactor, parallel plate denuder, and particle supersaturation chamber, connected to the ion chromatography systems via several 20 m perfluoroalkyl sampling lines carrying the dissolved analytes (Markovic et al., 2014). This design reduces artifacts by minimizing the inlet surface area prior to scrubbing the NH$_3$ from the gas phase in the denuder, and by separating the gas and particle phase constituents while the sample flow is still at ambient temperature and relative humidity (Markovic et al., 2012). In addition, size-resolved, sub-micron non-refractory NH$_4$$^+$ measurements were taken at 5 minute intervals using an Aerodyne Aerosol Mass Spectrometer (AMS, Liu et al., 2012). We averaged these data to 1 h time resolution in order to compare to the hourly CMAQ model output, which allowed for the evaluation of the ability of CMAQ to simulate the diurnal cycle of NH$_3$ concentrations. When NH$_4$$^+$ measurements are available, we compare model results to NH$_x$ to reduce our sensitivity to gas-to-particle partitioning errors in the model; otherwise we compare to NH$_3$$_3$.

2.3 TES NH$_3$ retrievals

During CalNex, TES made special observations (transects) near the Bakersfield, CA surface site with a horizontal separation of 12 km on six different afternoons. TES is a nadir-viewing Fourier-transform infrared (FTIR) spectrometer with a high spectral resolution of 0.06 cm$^{-1}$ and a nadir footprint of 5.3 km x 8.3 km. TES flies aboard the NASA Aura spacecraft, which is in a sun-synchronous orbit with an equator crossing time around 01:30 and 13:30 local solar time. Beer et al. (2008) reported the first satellite observations of boundary layer NH$_3$$_3$ using the TES instrument. Shephard et al. (2011) developed and tested a full NH$_3$$_3$ retrieval algorithm. The retrieval is based on an optimal estimation approach that minimizes the differences between the TES Level 1B spectra and a radiative transfer calculation that uses absorption coefficients calculated with the AER line-by-line radiative transfer model LBLRTM (Clough et al., 2006). The a priori profiles and covariance matrices for TES NH$_3$ retrievals are derived from GEOS-Chem model simulations of the 2005 global distribution of NH$_3$.

The TES NH$_3$$_3$ retrievals generally have a region of maximum sensitivity between 700 hPa and the surface. While the retrieval is performed on 14 pressure levels, the number of degrees of freedom for signal (DOFS) is generally not greater than one. Therefore at any given single profile level the retrieved volume-mixing ratio (VMR) of NH$_3$ is highly influenced by the a priori profile. Rather than attempting to analyse data from individual retrieval levels, it is often desirable to express
the retrieved information in a representation where the influence of the a priori is reduced and the information available is collapsed to a single point. To address this issue, Shephard et al. (2011) developed a Representative Volume Mixing Ratio (RVMR) metric for NH$_3$ based on similar techniques used previously for CH$_4$ (e.g., Payne et al., 2009; Wecht et al., 2012; Alvarado et al., 2015) and CH$_3$OH (e.g., Beer et al., 2008). This RVMR represents a TES sensitivity weighted average value where the influence of the a priori profile is reduced as much as possible; it generally ranges from 20% to 60% of the retrieved surface value for NH$_3$. The minimum detection level for TES NH$_3$ retrievals is an RVMR of approximately 0.4 ppbv, corresponding to a profile with a surface-mixing ratio of about 1-2 ppbv (Shephard et al., 2011).

Pinder et al. (2011) showed that the TES NH$_3$ retrievals were able to capture the spatial and seasonal variability of NH$_3$ over eastern North Carolina and that the retrievals compared well with in situ surface observations of NH$_3$, while Alvarado et al. (2011) showed that TES NH$_3$ retrievals can also capture the higher concentrations of NH$_3$ in forest fires in Canada. Sun et al. (2015) demonstrated that under optimal conditions (i.e., good thermal contrast and NH$_3$ amounts significantly above the TES level of detectability), TES NH$_3$ agreed very well with in situ aircraft and surface measurements taken in the California Central Valley during the DISCOVER-AQ 2013 campaign.

There are at least three issues that have to be considered when using NH$_3$ satellite profiles to evaluate model predictions: (a) the vertical resolution of the satellite profile is substantially coarser than that of the model profile; (b) the DOFS for NH$_3$ are generally less than 1.0; and (c) the retrieved satellite profile reflects the influence of the choice of a priori profile (Rodgers and Connor, 2003). Thus, in order to use these TES observations to evaluate CMAQ model predictions of the concentrations of NH$_3$, we first interpolate the hourly CMAQ NH$_3$ profile predicted for 13:00 local solar time (expressed as the natural logarithm of the mixing ratio) to the TES pressure grid. We then apply the TES observation operator to the interpolated CMAQ NH$_3$ profile to derive a model TES profile ($x_{TES}$). Finally, we apply the sensitivity weighting to calculate the model RVMR ($CMAQ_{RVMR}$). This value represents the RVMR that would have been retrieved if (a) TES had sampled a profile identical to the CMAQ-simulated profile and (b) the retrieval errors due to jointly retrieved parameters, other model parameters, and instrument noise were negligible. The observation operator equation is

$$x_{TES} = x_a + A(x_{CMAQ} - x_a)$$

and the RVMR is calculated as

$$CMAQ_{RVMR} = W \cdot x_{TES}$$

where $x_a$ is a vector of the TES a priori NH$_3$ concentrations, $A$ is the averaging kernel matrix, $x_{CMAQ}$ is a vector of the interpolated CMAQ NH$_3$ values, and $W$ is a weighting vector (Rodgers and Connor, 2003; Shephard et al., 2011). $W$ basically weights each level according to the sensitivity of the TES instrument at that level. It is calculated by summing the most significant rows of the averaging kernel at each level (see the appendix in Shephard et al., 2011 for details).
Several studies have used lidar observations of aerosol profiles to determine the height of the planetary boundary layer (PBL) by identifying regions of large gradients in aerosol concentrations with height (e.g., Tucker et al., 2009; Lewis et al., 2013; Scarino et al., 2014; Hegarty et al., 2015). Scarino et al. (2014) and Tucker et al. (2009) define the mixed layer measured by the HSRL as ‘the volume of atmosphere in which aerosol chemical species emitted within the boundary layer are mixed and dispersed’. The NASA Langley Research Center (LaRC) airborne HSRL measured mixed layer heights during the CalNex campaign and the Carbonaceous Aerosol and Radiative Effects Study (Scarino et al., 2014), both of which we used in this study.

3 Models

3.1 WRF-ARW

CMAQ v5.0.2 was driven with meteorology provided by WRF ARW Version 3.5 (Skamarock and Klemp, 2008) that was configured with 3 nested domains of 36, 12, and 4 km horizontal grid spacing and 41 vertical layers. Shortwave and longwave radiation were calculated using the Rapid Radiative Transfer Model code for General Circulation Model applications (RRTMG, Mlawer et al., 1997; Iacono et al., 2008). The YonSei University (YSU, Hong et al., 2006) non-local turbulent PBL scheme and the Noah land surface scheme (Chen and Dudhia, 2001) were used. Initial and boundary conditions for WRF were provided by the North American Regional Reanalysis (NARR, Mesinger et al., 2006), which is recognized as state-of-the-science for North America (Bukovsky and Karoly, 2007). The WRF runs were 32-hour simulations initialized every 24 hours at 0000 UTC with analysis nudging of winds, temperature and humidity above the PBL on the outer 36 km domain only, as in Nehrkorn et al. (2013). The WRF outputs for UTC hours 09:00 to 32:00 from each consecutive simulation were combined to form a continuous time series and the initial 8 hours of each simulation were discarded as spin-up time. The 8-h spin-up time and 32-h simulation length is longer than the 6-h spin-up time and 30-h simulation length used by Nehrkorn et al. (2013), but were necessary to perform 24-hour daily CMAQ runs using the 24-h daily CARB emissions files that started at 8:00 UTC. The WRF output was then converted to CMAQ-model-ready files using the Meteorology-Chemistry Interface Processor version 4.2 (MCIP).

3.2 CMAQ

We ran CMAQ on the inner 4 km WRF domain using the SAPRC07 chemical mechanism (Hutzell et al., 2012, Carter et al., 2010ab), which corresponds to the model-ready emission files for CalNex provided by CARB, and with the CMAQ AERO6 aerosol module with aqueous chemistry. Biogenic emissions, photolysis rates, and deposition velocities were all calculated inline. There were few clouds in California during this study period and thus lightning NOx emissions were negligible; however, lightning NOx emissions were also calculated inline in CMAQ. Initial and horizontal boundary conditions for
CMAQ were provided by GEOS-Chem simulations on a 2° x 2.5° latitude-longitude grid for May and June 2010 following the approach of Lapina et al. (2014). CMAQ emissions inputs for the state of California were provided as model-ready files by CARB, which prepared them using the Modeling Emissions Data System on a 4 km x 4 km grid-scale (available at http://orthus.arb.ca.gov/calnex/data/calnex2010.html, last accessed June, 2016). The emission change log is provided at ftp://orthus.arb.ca.gov/pub/outgoing/CalNex/2010/modelready/Change Log for Posted Inventories.pdf (last accessed June, 2016). In this inventory, the NH3 emissions in SJV are assumed to be constant throughout the day (i.e., no diurnal cycle), and are constant day-to-day in a given month. While emissions do vary month-to-month, we do not explore seasonal variation in this study, since the measurement campaign only occurred during the months of May and June. As the CARB model-ready files had no out-of-state emission sources, our initial simulations were run using the CARB emissions for California, the GEOS-Chem boundary conditions, and no out-of-state emissions. We quantified the potential error in gas-phase NH3(g), Aitken and Accumulation mode aerosol NH4(p), and NHx in the SJV from neglecting out-of-state agricultural NH3 emissions by using the agricultural NH3 emissions from the NEI2011 platform, which we re-gridded from 12 km to our model’s 4 km scale while keeping California state emissions constant. We performed this sensitivity test for a 7-day case study between 25-31 May with a 4-day spin up. Adding these out-of-state emissions had a negligible impact on the modeled NH3 concentrations in the SJV (less than 0.001 % change), as the prevailing winds are mostly out of the north and northwest. Additionally, we tested the effect that errors in the boundary conditions from GEOS-Chem might have on the model runs. Doubling NH3 boundary conditions for the same 7-day case study also had little impact on NH3 concentrations in the SJV (less than 0.001 % change), which was expected based on the short lifetime of NH3. Finally, we also ran CMAQv5.0.2 using the bi-directional NH3 flux scheme as developed by Bash et al. (2013) that uses fertilizer application data, crop type, soil type, and meteorology from MCIP output to calculate soil emissions potential and NH4 to simultaneously calculate NH3 deposition and emission fluxes for the CMAQ US domain. This scheme uses the U. S. Department of Agriculture’s Environmental Policy and Integrated Climate (EPIC) model (Cooter et al., 2012) as contained in the Fertilizer Emissions Scenario Tool (FEST-C).

In order to evaluate CMAQ v5.0.2 modeled NH3 in the SJV we ran three different scenarios for a month-long case study that covers the record of the Bakersfield surface observations (May 22 – June 22, 2010). The model scenarios include: 1) a baseline model run (CMAQbase), in which the model was set up as described above, utilizing the CARB emissions inventory; 2) CMAQp, which ran with the baseline set up but also included the bi-directional NH3 scheme described in Section 3.2, and finally 3) CMAQdp, which included both the bi-directional NH3 scheme and diurnally-varying emissions in the SJV, as described in Section 4.1.

3.3 HYSPLIT

In order to explore the sources influencing the Bakersfield concentrations we ran the HYSPLIT model. Using meteorological inputs from the WRF 4 km domain discussed in Section 3.1, we generated 36-hour back trajectories with Version 4 of the
HYSPLIT model (Draxler and Hess, 1998) initiated from 100 m above ground level (agl) at Bakersfield at 17:00 PDT on June 18th back to 20:00 PDT on June 17th. Results from these runs are briefly discussed in Section 4.1 and shown in Figure S1.

4 Model Evaluation

The following subsections describe the evaluations of all three-model scenarios using the three different measurement datasets from the CalNex campaign. Section 4.1 describes the modeled evaluation using surface measurements. Section 4.2 using the aircraft measurements and finally Section 4.3, utilizing the TES satellite measurements.

4.1 Evaluation of modeled transport and diurnal variability of NH$_{3(g)}$ using surface observations

Table 1 shows that the CMAQ$_{base}$ scenario has a NH$_3$ positive mean bias (MB) of 8.24 ppbv and a mean normalized bias (MNB) of 72.5% over the month-long surface data record; we focus on NH$_3$ so as to minimize the effects of possible model errors in gas-to-particle partitioning on our analysis, as discussed later in this section. NH$_3$ has a slightly higher bias, with NH$_{3(g)}$ having a lower MB of -0.40 ppbv, which has a small influence on total NH$_3$. However, this bias is not constant throughout the day, as can be seen in the CMAQ$_{base}$ results (blue line) shown in Figure 2. Figure 2a shows the average hourly ratio of CMAQ$_{base}$ modeled NH$_3$ versus measured concentrations for the Bakersfield ground site, averaged over all days of the CalNex campaign; these ratios are derived from the boxplots shown in Figure 2b. The model bias shows a clear diurnal cycle, with CMAQ$_{base}$ significantly overestimating surface NH$_3$ concentrations at night by up to a factor of 4.5 and generally underestimating NH$_3$ during the daytime by a factor of 0.6 between 13:00 and 14:00 local time, consistent with the average TES$_{RVMR}$ observations near Bakersfield at about 13:30 local solar time, which are plotted as the green dot in Figure 2a and further discussed in Section 4.3. These results suggest that constant daily agricultural NH$_3$ emissions in the CARB inventory (blue line Figure S2 in the Supplemental Material) may be misrepresenting the observed diurnal emission patterns. This is consistent with previous work done in North Carolina; Wu et al. (2008) found that NH$_3$ emissions from livestock feed lots show a strong diurnal cycle, peaking at midday.

Besides errors in emissions another contributing factor to the modeled bias of NH$_{3(g)}$ could be errors in gas-to-particle partitioning of NH$_{3(g)}$ to NH$_{3(g)}$ Figure 2a also shows that there is very little difference between the NH$_3$ (solid blue) and NH$_{3(g)}$(dashed-blue) lines, indicating only a small fraction of total NH$_{3(g)}$ is converted into NH$_{3(g)}$ in this region, consistent with Baker et al. (2013). Thus, errors in gas-particle partitioning of NH$_3$ in CMAQ, while important for accurately estimating PM$_{2.5}$ concentrations, cannot account for the diurnal errors in NH$_3$, we have observed.

Another potential source of diurnal errors in modeled NH$_3$ are diurnal variations in meteorology, which could alter the source regions to which the Bakersfield site was sensitive throughout the day. Differences between modeled and true NH$_3$ emission errors at upwind sites would thus appear as diurnal errors in NH$_3$. We ran a HYSPLIT case study for June 18th, where back trajectories were run for eight different times during the day (Figure S1). During the CalNex campaign, the...
During the nighttime there is a shift in wind direction to sources coming from the southeast. Cooling air from up in the eastern mountain ranges causes a mountain drainage effect into the southern valley area. This interaction of the mountain drainage combined with the typical low-level jet from the northern central valley creates a Fresno Eddy, as described in Michelson and Bao (2008). Figure 3 shows a wind rose for all points included in Figure 2, where measured wind direction and NH₃ concentrations are shown on the left, and modeled wind direction and NH₃ concentrations are shown on the right. It can be seen in Figure S5a that the nighttime wind measurements from the southeast generally have lower wind speeds (< 4 m s⁻¹) and that the model does not capture the variation of these wind speeds very well. This may be due to some timing errors in that the model may not capture true winds within a 4 km grid box, which corresponds to about 1-2 hours in real time. In general, many of the higher modeled NH₃ concentrations appear to be occurring during nighttime when the model should have winds out of the southeast, thus there is large model bias for these points. As indicated by the performed HYPLIT back-trajectories, and the description of air flow in the southern valley, we assume that although the measurements indicate the immediate wind direction was out of the south-east, the air-mass’s long-range transport still travelled over the Central Valley to accumulate emissions from that region before being recirculated by the Fresno Eddy to eventually come from the southeast. Thus, an overestimate of emissions in the Central Valley at night could still contribute to a model overestimate of measurements coming out of the southeast, rather than this air mass having come from a cleaner source, east of the mountains. Additionally, for the remaining time periods and majority of measurements not out of the southeast at nighttime, the model does a better job at simulating wind speeds (Figure S3), with a large model bias in NH₃ concentrations remaining. Thus, diurnal changes in transport are likely not the only contributing factor to the diurnal mismatch shown in modeling results.

Diurnal errors in the PBL height estimates could also be responsible for the diurnal error pattern in the CMAQ NH₃ concentrations at Bakersfield (Figure 2). We used daytime HSRL measurements taken in the SJV during CalNex to evaluate our WRF simulated PBL heights. Figure 5 shows 2-minute averages of the HSRL calculated mixed layer height compared to the WRF PBL for three daytime flights that passed over the SJV. The modeled and measured heights show good agreement, with a slope of 0.76, r² of 0.70, and mean bias of 87 m. Thus errors in daytime PBL height do not seem to account for much of the underestimate in modeled daytime NH₃. Scarno et al. (2014), when comparing all CalNex HSRL flight measurements to their configuration of the WRF-Chem model, found similar results. In summary, gas-to-particle partitioning and PBL height errors are likely not responsible for the diurnally varying measurement to model biases.

CARB NH₃ emissions in the SJV are constant both diurnally and day-to-day, with an hourly flux of around 0.23 moles s⁻¹ for the Bakersfield area (Figure S2). The Bakersfield ground measurements, however, indicate there should be a diurnal pattern of lower emissions at night and higher emissions during the day, as has been previously reported of NH₃ emissions from livestock (e.g., Bash et al., 2013; Zhu et al., 2015a) and other agricultural NH₃ sectors (Skjøth et al., 2011). The intense agricultural activities in the SJV generate large NH₃ emissions, with concentrations often exceeding 5 ppb as indicated in the ground measurements, making this an NH₃ rich region relative to the ambient sulfate concentrations. In this regime, since...
there is not enough sulfate to react with all the NH$_3$, a simple box model over the Bakersfield site, with wind speed, deposition, and PBL height variation held constant, would show a linear relationship between additional NH$_3$ emissions and the NH$_3$ concentration (Seinfeld and Pandis, 2006). Thus we expect errors in other parameters (PBL height, deposition, etc.) to affect modeled NH$_{SO2}$ and NH$_3$ concentrations to a greater degree, and we investigate these parameters below.

To test our hypothesis that the diurnal errors in NH$_3$ concentrations are due to diurnal errors in NH$_3$ emissions we explored two additional model scenarios to attempt to improve the diurnal cycle of NH$_3$ emissions in the CMAQ model. We found that including the bi-directional flux of NH$_3$ in the CMAQ$_B$ case (green lines) significantly reduces the nighttime concentration peaks of ground-site measured NH$_3$. However there is still a clear model NH$_3$ overestimate overall (MB of 4.57 ppb and large MNB of 45.74 %, see Table 1), and the low correlation is not improved ($r^2 = 0.011$). The CMAQ$_B$ scenario also shows overestimates following the day’s maximum in temperature (Figure 4). At night this bias is reduced relative to the total concentrations.

We then applied a scaling factor to all NH$_3$ area sources per grid box in the SJV, based on the CMAQ$_{max}$ bias relative to the ground measurements. To do this, we first calculated the total NH$_3$ area source emissions for each grid box, based on additional information on the emissions breakdown from the CARB inventory. For Kern County, where Bakersfield, CA resides, pesticide/fertilizer applications dominate the NH$_3$ emissions inventory at 72%, followed by farming operations (that include handling of all livestock and excrement) at 25%, and other sources for the remaining fraction. Table S2 in the Supplemental Material describes the fraction of NH$_3$ emissions for counties in the SJV. We then calculated the emissions for each hour based on the hourly average ground measurements and considering the NH$_3$-rich conditions. Note that the adjusted maximum emissions vary by about a factor of 4.5 from the minimum at night to the midday peak, as can be seen in Figure S1 (solid red line) which is more modest than the factor of 10 variation seen in livestock feedlots (Bash et al., 2013; J. Bash, personal communication, Oct. 6, 2015). We then reran CMAQ with both these adjusted emissions and the bidirectional NH$_3$ scheme (the CMAQ$_{ab}$ run) to assess the impact. Despite applying the scaling factor to all emissions instead of solely to the feedlots as in Bash et al. (2013), the CMAQ$_{ab}$ model predictions, shown as the purple lines in Figure 4, matches the measurements (black line) better than the CMAQ$_{max}$ or CMAQ$_B$ scenarios over the day and night, with large outliers seemingly reduced, consistent with Bash et al. (2013). The mean nighttime bias for CMAQ$_{ab}$ was reduced by about a factor of 2 and the overall bias of NH$_3$ reduced to -1.23 ppbv (Table 1); this model version does particularly well between the hours of 01:00 and 06:00 (see Figure). The fact that adding the diurnally-varying emission profile reduces the model bias, even though the emissions are dominated by fertilizer applications that should be accounted for by the bi-directional NH$_3$ scheme, suggests that the bi-directional NH$_3$ scheme in CMAQ v5.0.2 is not correctly accounting for the diurnal variations in NH$_3$ flux in the SJV. Furthermore, when we compare the modeled NH$_3$ to measured values coming from just the southeast at night (Figure S5), the model bias is reduced by about factor of 3.5. This suggests that although the model may not capture the immediate wind direction and wind speed at night, as explained above, because of the long-range transport down the Central Valley that evolves into the Fresno Eddy, reducing emissions in this upwind region also reduces model bias for these.
points in time. However, we note that the correlation of all three-model scenarios remains very low ($r^2 < 0.06$), suggesting further model errors, such as the neglect of any day-to-day variation in NH$_3$ emissions in our simulations.

As noted above, the results for NH$_{3,sp}$ generally track the results for NH$_3$ already discussed. In contrast, the model usually under-predicts the small amount of NH$_{3,sp}$ observed (on average < 1 ppbv, Figure 4c) by a factor of 2, with little variation between the model scenarios (Table 1). MB of NH$_3$, for CMAQ$_{basex}$, CMAQ$_b$, and CMAQ$_{AB}$, is -0.40, -0.41 and -0.44 respectively. These model errors in NH$_{3,sp}$ reflect not only model errors in total NH$_3$, but also errors in the formation of HNO$_3$ and SO$_2$ (Figure S3). HNO$_3$ is overestimated in all model simulations up to a factor of 4, with concentrations not changing between model cases. SO$_2$ measured concentrations are minimal and do not appear to have any trend and also do not change with model cases. However, as our interest in this study is in constraining NH$_3$ emissions, not inorganic aerosol formation, we do not investigate these errors further here.

4.2 Evaluation of modeled vertical distribution of NH$_{3,sp}$ using aircraft observations

The aircraft observations in the SJV indicate a large underestimate (range of factors about 1 to 5) in CMAQ$_{basex}$ modeled NH$_3$ concentrations above the surface, as shown in Table 2 (all flights in SJV) and Figure 5 (two flights). The variation in model concentrations in the background of Figure 6 are due to the aircraft flying in and out of different horizontal grid boxes in the model. The May 24th flight shows a strong CMAQ$_{basex}$, NH$_3$ underestimate of about a factor of 5 when considering the entire flight with a low correlation ($r^2$) of 0.31 and a mean bias of -1.95 ppbv. This significant underestimate could potentially be due to an underestimate of vertical mixing at night (discussed below); when only data before 18:00 PDT is considered (assuming this is before the collapse of the convective boundary layer) the underestimate is only a factor of ~1.5 and the $r^2$ is 0.77, a considerably better and statistically significant result. However, model comparisons to flight data on 16 and 18 of June before 18:00 PDT, likely before the boundary layer collapse on these days, show a significant model underestimate and low $r^2$ values. Thus, there may be other contributing factors to this bias and lack of correlation, such as errors in vertical transport and neglect of day-to-day variability in the emissions.

A daytime vs evening flight measurement evaluation of CMAQ$_{basex}$ shows a clear difference in the vertical distribution of NH$_3$. At night (May 24th flight, Figure 6b), the model contains most of the NH$_3$ in the lowest model level, whereas during the day (June 16th flight) it vertically mixes the NH$_3$ (Figure 6a). Based on the higher NH$_3$ concentrations that the aircraft is measuring these results could suggest 1) vertical mixing is stronger than simulated in the model during both day and night flights or 2) that there is a residual layer of NH$_3$ at night that is not captured by the model or 3) there is a non-local source that is also not well captured by the model.

Gas-phase NH$_3$ can either be deposited to or emitted from the surface depending on the land-type, land-use, and ambient concentrations (Bash et al., 2015; Fowler et al., 2009). The CMAQ$_{basex}$ run does not take this into consideration, but when bi-directional NH$_3$ is calculated with a diurnal emission factor included in CMAQ$_{basex}$, NH$_3$ dry deposition should generally decrease, increasing the net land-atmosphere flux (Bash et al., 2013). The CMAQ$_{AB}$ model run shown in Figure 6c is consistent with these results (and inconsistent with the hypothesis that vertical mixing is underestimated in the model) as the
vertically distributed concentration of NH₃ significantly increases from the CMAQ₃₀ case to the CMAQₓ₀ case. The transport of NH₃ also seems to increase, this being a potential explanation for the plume entering the plot domain around 21:00 PDT in the bottom curtain plot. The total column concentration of NH₃ also increases, leading to a significant positive model bias for the CMAQₓ₀ scenario (e.g. in the earlier part of the flight in Figure 5c and Table 2), suggesting a possible overestimation of total NH₃ emissions by the bi-directional NH₃ scheme and further enhanced by adding a diurnal emission factor during the afternoon and evening hours when the flights took place. This indicates that the diurnal factor application in NH₃ emissions at the surface grids does not significantly change the concentrations aloft, where the flight measurements are taking place compared to the CMAQₓ₀ case, resulting in remaining model bias and requiring further investigation.

4.3 Evaluation of modeled NH₃ with TES NH₃ retrievals

Applying the TES operator to the CMAQ profiles and calculating the CMAQₓ₀-VMR allows us to compare the satellite and model datasets quantitatively, as described in Section 2.3. Surface NH₃ from the CMAQ₃₀ run (Figure 7a) and the TES NH₃ RVMR (Figure 7b) along a sample TES transect both identify the regions of large NH₃ sources and the spatial changes along the transect and demonstrate that the CMAQₓ₀ is underestimated for the base run, particularly at higher NH₃ RVMRs. Similar results were found for other transects and summarized in Table 3 and Table S2. The time of the satellite overpass occurs just prior to the peak of emissions in the emission factor applied to the CMAQ₃₀ case which in turn increases the RVMR bias to 1.31 ppbv and increases the regression slope to 1.02 (purple line Figure 8) as compared to a bias of -2.57 and slope of 0.40 in the CMAQₒ case. The slope of the linear regression of CMAQₓ₀ RVMR suggests that CMAQ run with bi-directional ammonia along with the applied emissions factor slightly overestimates NH₃ concentrations, indicating the magnitude of the emissions factor may be too high at the time of satellite over pass. The inclusion of the emission factor in this CMAQₓ₀ case has a higher bias than the bi-directional model run, CMAQₒ. This demonstrates the importance of using highly time-resolved observations of NH₃ to determine the diurnal cycle of NH₃ along with polar-orbiting satellite retrievals of NH₃ to improve the spatial and seasonal distribution of the emissions, as noted in Zhu et al. (2013). In other words, if we had relied solely on the TES observations at 13:30 local solar time to evaluate the CMAQₓ₀ runs, we would have incorrectly assumed that the CARB inventory was a factor of 2.4 too low for total NH₃ emissions, whereas the surface data demonstrate that the problem is primarily in the diurnal cycle of the emissions.

Modelled RVMR can be very sensitive to errors in the modeled vertical distribution of NH₃. We investigated this by comparing each level of the TES retrieved NH₃ profile with the corresponding CMAQ profile level after the observation operator is applied. Figure 9 shows box-and-whisker plots of this comparison for the CMAQₒ and CMAQₓ₀ model scenarios (CMAQₒ not shown). This plot differs from that in Shephard et al. (2015) in that it includes the average of layers below 908 mb, which introduce an RVMR bias due to levels that are below 1000 mb. The CMAQₓ₀ case shows the smallest bias of the three modeled scenarios in the lowest pressure level (~1 ppb) with the higher levels showing little bias as well (~0.08 ppb). Thus comparing the TES and CMAQ profiles level-by-level indicates that the CMAQₓ₀ scenario demonstrates
5 Discussion

The results in Section 4 show that the CMAQ\textsubscript{AB} model scenario that included both the bi-directional NH\textsubscript{3} scheme and the diurnally adjusted emissions provided results that were much closer to the surface measurements (Section 4.1) and satellite (Section 4.3) observations than the CMAQ\textsubscript{base} runs, with measurement uncertainties explained in Section 2. The CMAQ\textsubscript{AB} simulations did result in a large overestimate of NH\textsubscript{3} concentrations higher in the atmosphere as measured by the aircraft (Section 4.2). Here we discuss the remaining errors in the CMAQ\textsubscript{AB} scenario, suggest possible explanations for these errors, and make suggestions for the direction of future research.

Model bias in both the night and daytime simulation of surface NH\textsubscript{3} is reduced in the CMAQ\textsubscript{AB} scenario. The total bias is significantly reduced from the factor 4.5 at night and 0.6 during the day compared to the CMAQ\textsubscript{base} scenario (Figure 4a). In CMAQ\textsubscript{AB}, the model does well between the hours of 1:00 am and 6:00 am local time (Figure 4c), perhaps related to the lower emissions at this time of day when adjusted emissions are used assuming the linear relationship of emissions to concentrations. The remaining diurnal bias shows a relative model underestimate with a factor of ~0.6 at 10:00 local time and a relative model overestimate peaking at ~1.7 at 19:00 local time (Figure 4c), with average CMAQ\textsubscript{AB} modeled concentrations slightly higher in the afternoon and peaking around 19:00 (Figure 4d). It is interesting to note that the CMAQ\textsubscript{AB} bias relative to surface concentrations is small near the TES overpass time (e.g., crossing 0% between 13:00 and 14:00 local time, Figure 4e), which is consistent with the small bias seen in the comparison with the TES observations in Section 4.3. Furthermore, the aircraft results for the CMAQ\textsubscript{AB} scenario discussed in Section 4.2 also show a large relative overestimate in the afternoon and evening when the flights took place (Table 2), consistent with the afternoon and evening overestimates seen in the surface data.

Thus all three datasets suggest that the remaining errors in modeled NH\textsubscript{3} concentrations may be due to the diurnal profile of the net land-atmosphere NH\textsubscript{3} flux in the CMAQ\textsubscript{AB} run peaking too late in the day. One possibility is that the diurnal cycle applied to the non-fertilizer NH\textsubscript{3} emissions, which was based on the ambient measurements of NH\textsubscript{3}, is peaking too late in the day. However, as the peak of our assumed diurnal profile for these emissions (Figure S1) is consistent with the peak in surface temperature (1:00 pm, Figure 4d), we consider this explanation less likely than remaining errors in the bi-directional NH\textsubscript{3} scheme for fertilizer emissions.

These errors in the bi-directional NH\textsubscript{3} scheme could be due to errors in the dynamic emissions response of the bi-directional NH\textsubscript{3} scheme to local temperature, wind direction and speed (Bash et al., 2013). However, Figure 4d shows that the modeled surface temperature and wind speed are not that far off from the values observed at the Bakersfield site for the majority of measurements out of the northwest, and for those out of the southeast that are not captured in the model, we believe that the long-range transport of these winds through the Central Valley prior to entering the Fresno Eddy are dominating the
emissions profile of that air mass, thus influencing the final concentration of that air mass. Thus the remaining errors are less likely related to errors in atmospheric meteorological conditions, and are more likely due to errors in the land-air interactions and the dependence of soil conditions (e.g., soil temperature, pH, and water content) on meteorology and crop management practices as calculated within the bi-directional NH$_3$ scheme (Cooter et al., 2012). The scheme calculation assumes two soil layers (0.01 m and 0.05 m) that independently exchange NH$_3$ with the canopy, which then exchanges NH$_3$ with the surface layer of the atmosphere (Bash et al., 2013). If the calculation of the response of soil properties in these layers to surface meteorology and crop management practices is incorrect (e.g., the soil layers do not heat up or cool down quickly enough with the change in surface temperature), that would affect the amount of NH$_3$ available from the soil as well as the rate at which the soil NH$_4^+$ is converted to NO$_3^-$ through nitrification (Bash et al., 2013). This would result in errors in the flux of NH$_3$ from the soil to the canopy, thus altering the canopy compensation point and the net atmospheric flux.

The aircraft results may also suggest errors in the vertical mixing of NH$_3$ during the afternoon and evening (e.g., the peak of the PBL height and the collapse). While we consider this effect as likely less important to the remaining errors in CMAQ$_{AB}$ than the potential errors in the bi-directional NH$_3$ scheme already discussed, an overestimate of vertical mixing during the afternoon would overestimate the flux of NH$_3$ from the surface layer of the atmosphere to the upper levels, reducing the concentrations, which is consistent with the aircraft overestimate. In addition, the soil-canopy-surface atmosphere system would respond to this overestimate of vertical mixing by increasing the net flux of NH$_3$ from the soil to the atmosphere in order to maintain equilibrium, resulting in a total overestimate of the emissions of NH$_3$ during the afternoon and evening.

We thus recommend that future work to improve the simulation of atmospheric NH$_3$ concentrations in the SJV focus on bottom-up and top-down approaches that will better estimate the diurnal changes in the canopy compensation point that determines the net flux from the land to the atmosphere in the bi-directional NH$_3$ scheme (Bash et al., 2013). This scheme was originally developed using field scale observations taken in North Carolina, USA (Walker et al., 2013), so it is not surprising that this approach may require modifications to work in the SJV. We recommend, first, that the CARB NH$_3$ inventory be updated to better separate NH$_3$ emissions from fertilizer and livestock sectors. The Bash et al. (2013) scheme assumes that these two sectors will dominate NH$_3$ emissions, while the CARB inventory divides fertilizer/pesticide use from “farming operations”, thus it is unclear if these other farming practices are dominated by livestock or not. Second, crop management data (e.g., fertilizer amount, timing, form, and distribution) used in EPIC (and thus in the CMAQ bi-directional NH$_3$ scheme) are based on data for the entire West Coast of the US (e.g., California, Oregon, and Washington), and thus may not be representative of farming practices in the SJV. Better crop management data specific to the SJV, as well as more SJV-specific data on soil moisture and heating rates, may thus help in removing some of the remaining errors in the CMAQ$_{AB}$ scenario. Third, in order to better connect these bottom-up emission estimates to the measured atmospheric concentrations, we recommend that top-down studies focus not just on correcting the net NH$_3$ flux to the atmosphere but also determine the diurnally-varying biases in the canopy compensation point that determines these net fluxes. This may require the development of adjoint methods and models (e.g., Zhu et al., 2015a) that can retrieve time-varying correction factors for the canopy compensation point, rather than just for the net flux itself.
6 Conclusions

We used NH₃ retrievals from the NASA Tropospheric Emission Spectrometer, as well as surface and aircraft observations of NH₃, and submicron NH₄, gathered during the CalNex campaign, to evaluate the ability of the CMAQ model run with the CARB emission inventory to simulate ambient NH₃ and NH₄ concentrations in California’s San Joaquin Valley. We find that CMAQ simulations of NH₃ driven with the CARB inventory are qualitatively and spatially consistent with TES satellite observations, with a correlation coefficient (r²) of 0.64. However, the surface observations at Bakersfield indicate a diurnally varying model bias and low correlation, with CMAQ overestimating NH₃ at night by at times more than 50 ppbv and underestimating it during the day by up to 10 ppbv. The surface, satellite, and aircraft observations all suggest that the afternoon NH₃ emissions in the CARB inventory used in CMAQ are underestimated by at least a factor of two, while the nighttime overestimate of NH₃ is likely due to a combination of overestimated nighttime NH₃ emissions and underestimated nighttime deposition. Thus the diurnally-constant NH₃ emissions used by CARB in the SJV appear to misrepresent the diurnal emission cycle.

Using the bi-directional NH₃ scheme in CMAQ (CMAQ_B) resulted in reduced NH₃ concentrations at night and a slight increase during the day, overall reducing the model bias relative to the surface and satellite observations. However, this scenario substantially increased the simulated mixing ratio of NH₃, higher at high altitudes, leading to an increased bias relative to the aircraft observations. In addition, errors in the simulation of the nighttime surface concentrations remained in this scenario.

In order to evaluate the diurnal impact of NH₃ emissions, we used the surface observations at Bakersfield to derive an empirical diurnal cycle of NH₃ emissions in the NH₃-rich region of the SJV in which nighttime and midday emissions differed by about a factor of 4.5. Despite the model not capturing winds out of the southeast at night, adding a diurnal profile to the CMAQ bi-directional NH₃ simulations (CMAQ_B) while keeping the daily total NH₃ emissions constant at the CARB values significantly reduced the model bias at night relative to the surface observations, on top of the already reduced bias from the CMAQ simulation. Comparisons with the TES RVMR showed a slight increase in the bias for the CMAQ_B scenario relative to CMAQ, but further examination of the modeled and retrieved vertical profiles suggests that this is primarily due to ~1 ppb differences in the lowest retrieved level with the CMAQ_B scenario showing little bias (0.08 ppbv) relative to the TES NH₃ profile above this surface level. However, despite nighttime reduction in model bias in the CMAQ_B scenario sizable errors (up to 20 ppbv) in the afternoon and evening NH₃ and low model correlations remained, possibly due to the net land-atmosphere NH₃ flux calculated by the bi-directional NH₃ scheme peaking too late in the day due to errors in the calculated response of the soil conditions (e.g., soil temperature, pH, and water content) to meteorology and crop management practices.

We recommend that future work on modeling NH₃ emissions in the SJV include (a) updating the CARB NH₃ inventory to account for NH₃ from fertilizer, livestock, and other farming practices separately, (b) adding information on crop management practices specific to the SJV region to the EPIC-FESTC system, and (c) top-down studies that focus not just on
correcting the net NH₃ flux to the atmosphere but also on determining the diurnally-varying biases in the canopy compensation point that determines these net fluxes.
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References


Table 1: Summary statistics of the modeled NH₃, NH₃(g), and NH₄⁺ concentration comparisons to the ground measurements for all three model runs. Mean Bias (MB) = mean (modeled – measured), Mean Normalized Bias (MNB) = mean ((modeled – measured)/measured). Note that low r² values, less than 0.10, are highlighted in italics.

<table>
<thead>
<tr>
<th>Model Run</th>
<th>Slope</th>
<th>r²</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
</tr>
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<tbody>
<tr>
<td>CMAQ_base</td>
<td>-2.49+/-.15</td>
<td>0.001</td>
<td>8.24</td>
<td>72.54</td>
<td>8.65</td>
<td>78.79</td>
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<td>4.57</td>
<td>43.74</td>
<td>4.99</td>
<td>50.60</td>
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<td>-55.92</td>
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<tr>
<td>CMAQAB</td>
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<td>-1.23</td>
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<td>-0.79</td>
<td>-14.01</td>
<td>-0.44</td>
<td>-60.24</td>
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</tbody>
</table>

Table 2: Summary statistics of the modeled to measured NH₃ concentration comparisons following the SJV flights. Mean Bias (MB) = mean (modeled – measured), Mean Normalized Bias (MNB) = mean ((modeled – measured)/measured). Note that low r² values, less than 0.10, are highlighted in italics.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time (PDT)</th>
<th>Slope</th>
<th>r²</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
</tr>
</thead>
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<td>16:00-22:00</td>
<td>0.20+/-.01</td>
<td>0.31</td>
<td>-1.95</td>
<td>-2.010</td>
<td>-1.74</td>
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<td>-0.14</td>
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<td>0.68+/-.05</td>
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<td>-32.46</td>
<td>-0.08</td>
<td>-53.19</td>
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<tr>
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<td>0.29</td>
<td>-2.40</td>
<td>-0.213</td>
<td>-2.24</td>
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<td>-0.14</td>
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<tr>
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<td>20100616</td>
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<td>CMAQb</td>
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<td>5.56</td>
<td>351.82</td>
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<td>6.63</td>
<td>279.85</td>
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<td>4.41</td>
<td>458.88</td>
<td>-0.21</td>
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<td>474.89</td>
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<td>7.07</td>
<td>664.26</td>
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<td>330.05</td>
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<td>7.83</td>
<td>264.1</td>
<td>8.19</td>
<td>297.58</td>
<td>-0.22</td>
</tr>
<tr>
<td></td>
<td>20100618</td>
<td>13:00-18:00</td>
<td>0.42+/-.05</td>
<td>0.03</td>
<td>5.59</td>
<td>425.7</td>
<td>5.76</td>
<td>494.16</td>
<td>-0.21</td>
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</tbody>
</table>
Table 3. Summary statistics of the CMAQ<sub>RVMR</sub> to TES<sub>RVMR</sub> NH<sub>3</sub> comparisons for 4 CalNex overpasses (05/28, 05/30, 06/13, 06/15). Mean Bias (MB) = mean (modeled – measured), Mean Normalized Bias (MNB) = mean ([(modeled – measured)/measured].

<table>
<thead>
<tr>
<th>Model Run</th>
<th>Slope</th>
<th>r²</th>
<th>MB (ppbv)</th>
<th>MNB (%)</th>
</tr>
</thead>
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<tr>
<td>CMAQ&lt;sub&gt;b&lt;/sub&gt;</td>
<td>0.47</td>
<td>0.64</td>
<td>-2.57</td>
<td>-30.21</td>
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<tr>
<td>CMAQ&lt;sub&gt;B&lt;/sub&gt;</td>
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<td>0.60</td>
<td>0.84</td>
<td>14.40</td>
</tr>
<tr>
<td>CMAQ&lt;sub&gt;AB&lt;/sub&gt;</td>
<td>1.02</td>
<td>0.60</td>
<td>1.31</td>
<td>19.57</td>
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</table>
Figure 1. Distribution of NH$_3$ emissions across California (background) on May 12, 2010 at 19:00 UTC as well as P3 flight tracks (small circles), TES transect (green squares), and the Bakersfield site (red star) with the county lines shown in white.
Figure 2. (a) The average hourly ratio of modeled to measured NH$_3$ (dashed line) and NH$_x$ (solid line) mixing ratios at the Bakersfield ground site for the CMAQ$_{base}$ (blue), CMAQ$_B$ (green) and CMAQ$_{AB}$ (purple) cases, and the average modeled RVMR to TES RVMR ratio (green dot) in local time. (b) Boxplot of average hourly NH$_3$ mixing ratios at the Bakersfield ground site for the measured (black), CMAQ$_{base}$ (blue) and CMAQ$_{AB}$ (purple) cases, averaged over all measurement days during CalNex where the boxplots show the inter-quartile range and median line (red) within the box and outliers (whiskers), with the solid lines showing the mean for that day.
Figure 3. Wind rose of measured wind direction and NH\textsubscript{3} on the left, and CMAQ\textsubscript{AB} modeled wind direction and NH\textsubscript{3} on the right where contours represent number of data points (hourly) per wind direction. Note the difference in scale, where values are in ppb.
Figure 4. The CalNex ground measurements at the Bakersfield site (solid black) compared to the CMAQ_{base} (solid blue), CMAQ_{AB} (purple) and CMAQ_{B} (green) simulations for a month of model runs. The top panel (a) shows NH$_3$, b) shows NH$_3$ (g), c) NH$_4$ (p) and temperature (K) and d) wind speed on the left and wind direction on the right axis.
Figure 5. Time series of WRF predicted planetary boundary layer heights and HSRL calculated mixed layer heights for 3 flight sections in the San Joaquin Valley (2 during CalNex and one during a CARES campaign).
Figure 6. (a) The hourly output of CMAQ base NH$_x$ is shown in the background with the measured (one minute average) NH$_x$ concentrations within the modeled hour shown as the dots for the daytime flight on June 16, 2010 and (b) a nighttime flight on May 24, 2010, and (c) the same nighttime flight but for the CMAQ AB scenario.
Figure 7. NH$_3$ representative volume mixing ratios (RVMRs) on 12 May 2010 during the CALNEX campaign for (a) TES special observations, (b) modeled RVMR for CMAQ and (c) the difference between each RVMR near the Bakersfield, CA, surface site with the white diamond locating the Bakersfield measurement site.
Figure 8. Scatter plot of CMAQ_{base} (blue), CMAQ_{B} (green) and CMAQ_{AB} (purple) versus TES NH$_3$ representative volume mixing ratios for TES special observation passes (TES_{RVMR}) during the CalNex campaign with statistics discussed in Table 3.
Figure 9. Boxplots of a) TES NH$_3$ retrieval by pressure level, b) TES NH$_3$ retrieval averaging kernel (AK) diagonal, c) difference between the TES NH$_3$ retrieval and CMAQ base modeled NH$_3$ interpolated to TES levels with an AK applied for the baseline model run and d) same as Panel c but for the CMAQ$_{AB}$ run. Box plots show the mean (green), median (red), interquartile range (IQR, blue box), whiskers at 1.5 IQR and outliers beyond that.
Figure 2. The CalNex ground measurements at the Bakersfield site (solid black) compared to the CMAQ_{base} (solid blue), CMAQ_{AB} (purple) and CMAQ_{B} (green) simulations for a month of model runs. The top panel (a) shows NH_x, b) shows NH_3(g), c) NH_4(p), and d) wind speed on the left and temperature on the right axis.

Figure 3. a) The average hourly ratio of modelled to measured NH_3 (dashed-dotted line) and NH_x (dashed line) mixing ratios at the Bakersfield ground site and the average modelled RVMR to TES RVMR ratio (green dot) in local PDT. b) Boxplot of average hourly modelled (red) and measured (blue) NH_x mixing ratios for the Bakersfield ground site, averaged over all measurement days during CalNex where the boxplots show the inter-quartile range and median line within the box and outliers (whiskers).  
  ) The average hourly ratio of CMAQ_{AB} modelled to measured NH_x (dashed line) mixing ratios at the Bakersfield ground site  
  ) Boxplot of average hourly CMAQ_{AB} modelled (red) NH_x mixing ratios for the Bakersfield ground site.