

***Interactive comment on “Eta-CMAQ air quality forecasts for O<sub>3</sub> and related species using three different photochemical mechanisms (CB4, CB05, SAPRC-99): comparisons with measurements during the 2004 ICARTT study” by S. Yu et al.***

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We thank the anonymous referee #1 for the constructive and helpful comments, and the incorporation of which has led to a substantially improved manuscript.

Reviewer #1(Comments):

Major comments: The authors present a comparison of three different air quality model simulations against detailed measurements from an extensive field study. The simulations differ in their use of the chemical mechanism. Both the model simulations and

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the measurements are of high quality. The differences between the chemical mechanisms are summarized very well, and Tables 1-2 and 6 are very useful for reference and comparison purposes. The analysis of the model simulations and observations is generally sound.

Response: We thank the reviewer for the overall positive assessment of the manuscript.

However, I have some concerns about the organization of the paper and the interpretation of the results: - A fair amount of the information shown in the tables and especially in the vertical profiles is not discussed in the text. Examples of this are provided in the specific comments

Response: Thanks a lot for this comment. Some more discussions have been added in the revised manuscript as shown below.

- Throughout the text, but especially in the abstract and summary, the authors seem to highlight instances where CB05 performs best although overall none of the mechanisms performs systematically better than the others. This may be inadvertent but could lead to the impression that the results presented in this paper support the use of CB05 over other mechanisms which is not how I interpret the results. Instead, the main message I see emerging from the Figures and Tables is that these three mechanisms represent a range of uncertainty in the treatment of photochemistry. The reason for any “better” performance for a given mechanism, variable and metric could be manifold: the time and locations of the measurements (as manifested in the differences in model performance for a given mechanism and pollutant between the P3 and DC-8 datasets), uncertainties in meteorology (these simulations used a hydrostatic model that has been phased out by the NWS), uncertainties in anthropogenic and biogenic emission inventories (for example, if MEGAN had been used instead of BEIS, I suspect that Figure 1 would have shown best performance for CB4 for all regimes because ozone would have been increased as a result of increased isoprene). While the

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authors do acknowledge these confounding factors at times, at other times it appears that a case is being made for CB05 relative to CB4. In my judgment, that case is not supported by the data presented here.

Response: We totally agree with what the reviewer said. Overall none of the mechanisms performs systematically better than the others. The abstract has been rewritten in the revised manuscript.

- Given that a large part of the differences between the mechanisms stems from the treatment of hydrocarbons, it might be worth to include data from the PAMS network into the analysis.

Response: We thank the reviewer for this suggestion. We will include PAMS data into the analysis in the future work.

- For consistency with Figure 1, it would be nice to see the ozone model performance for the other platforms (aircraft, ship, AIRMAP) grouped by observed ozone concentration bins as well. This would entail performing the ozone analysis for these other platforms for daily maximum 8-hr data in addition to the hourly data currently used.

Response: We appreciate this comment. Since the observations from aircraft and ship are for the different locations along their tracks, we feel that it may be not a good idea to calculate the max 8-hr data for these data like those for the AIRNow sites. Regarding the ship data, we feel that the time-series plots like Figure 6 are a better way to present the results because these data have much high time resolution and we want to see the temporal variations of the data.

Specific Comments: Page 22,960, lines 10-21. The very limited analysis of the AIRMAP data shown in Section 3.3.1 does not support the statement “: : : a variety of tests were used to examine the influence of three photochemical mechanisms on simulating the processes governing the distributions of tropospheric O<sub>3</sub>”. This limited analysis (1 table, 1 paragraph) does not justify its classification as a separate objective

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of the study. The same concern applies to the analysis of the AIRNOW data which is not very comprehensive and may not warrant classification as a separate objective.

Response: We agree with the reviewer. To address the reviewer's concern, we have rewritten the objectives in the revised manuscript as follows: “The objective of this study is to assess the influence of the three photochemical mechanisms on the Eta-Community Multiscale Air Quality (CMAQ) model's ability to simulate O<sub>3</sub>, its related chemical species over the eastern United States with observations obtained by aircraft (NOAA P-3 and NASA DC-8) flights, ship and two surface networks (AIRNow and Atmospheric Investigation, Regional Modeling, Analysis, and Prediction (AIRMAP)) during the 2004 International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study.”.

Page 22,961, lines 11-13: I recommend not breaking up the presentation of reaction rates between Tables 1-2 and 6. In other words, Table 6 should be shown as Table 3.

Response: We agree with the reviewer. Table 6 has become a part of Table 2 in the revised manuscript.

Page 22,963, line 12: Isn't AIRNow a database containing measurements from various networks, not an actual network? Also, in my understanding data in the AIRNow database are preliminary and have not undergone the same level of quality assurance as the final measurements at these monitors that are stored in the AQS database. I would recommend to either use the ozone data retrieved from the AQS database or add a cautionary statement about the AQS database.

Response: Yes, we agree with the reviewer. AIRNow is a database containing measurements from various networks, but not an actual network. “AIRNow” instead of “AIRNow network” has been used in the revised manuscript. The AIRNow data are performed through some preliminary data quality assessments as stated in the AIRNow website ([http://www.airnow.gov/index.cfm?action=topics.about\\_airnow](http://www.airnow.gov/index.cfm?action=topics.about_airnow)). Since our project is to use Eta-CMAQ model to forecast air quality, the only near-real

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time data available are from the AIRNow. For the purpose of this work for evaluation of model performance, we feel that it is reasonable to use AIRNow data. AIRNow data cannot be used to formulate or support regulation, guidance or any other Agency decision or position. To address the reviewer's concern, the following sentence has been added in the revised manuscript "Note that AIRNow data have only gone through some preliminary data quality assessments".

Page 22,963, line 12: why is the number of hourly ozone observations mentioned even though the analysis is focused on 8-hr daily maximum ozone?

Response: We just want to show how many data we used in our study. To address the reviewer's concern, the sentence "resulting in nearly 1.2 million total hourly O<sub>3</sub> observations for the study period" has been deleted in the revised manuscript.

Page 22,963, line 17: The Ron Brown ship data should also be mentioned in this section.

Response: We agree. The following sentence "The observations of O<sub>3</sub> and its related chemical species along the coast of New Hampshire, Massachusetts and Maine were obtained by the NOAA ship Ronald H. Brown during the 2004 ICARTT field experiment" has been added in the revised manuscript.

Page 22,964, lines 3-4: Please clarify what is meant by "additional" insights into model performance? There are no results shown before this section. Please also state that the NMB is calculated for 8-hr DM ozone. This is stated in the Figure legend but not the text.

Response: We agree with the reviewer. "additional" has been removed and "for maximum 8-hr O<sub>3</sub>" has been added in the revised manuscript.

Page 22,964, line 5: suggest rephrasing " are calculated for three mechanisms as displayed" with "are calculated for three mechanisms and are displayed"

Response: Done.

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Page 22,963, Section 2.3 and Page 22964, Section 3.1: Suggest reordering the Figures: Figure 1b (map of station) first, followed by Figure 2 (flights and ship tracks), followed by Figure 1a (bar charts with ozone NMB results) to be consistent with the order in which they are discussed.

Response: Done.

Page 22,964, line 10-13: To support this statement, please provide the percentage of urban, suburban and rural sites used in this analysis.

Response: As we check on the basis of available information, the percentages of urban, suburban and rural sites used in this analysis are 18%, 41% and 41%, respectively. To address the reviewer's concern, the following sentence has been used in the revised manuscript "...because majority of the AIRNow sites are located in urban or suburban areas".

Page 22,964, lines 18-20: Please move the phrase "for all three mechanisms" between "was in the northeast" and "where very low O<sub>3</sub> mixing ratios were observed".

Response: Done.

Page 22,965, line 2: Figure 2 actually doesn't show that the flight tracks for the P3 range from altitudes of zero to five kilometers

Response: We agree with the reviewer. "from 0 to ~5 km altitudes" and "between 0 and 12 km altitudes" have been deleted in the revised manuscript.

Page 22,965, line 12: please define and then describe the "composite vertical variation patterns" for observations and model predictions

Response: We agree with the reviewer. "vertical variation patterns" has been used in the revised manuscript.

Page 22,965, lines 15-16: suggest adding "vertical" between "coarse" and "model"

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Response: Done.

Page 22,965, line 17: please replace “consistence” with “consistencies”

Response: Done.

Page 22,965, line 19: should this be “O3+NO2”, not “O3+NOZ”?

Response: Yes, you are right. “O3+NO2” has been used in the revised manuscript.

Page 22,965, lines 4-28: consider combining Figures 3 and 4. Also consider using a common layout for Figures 3-4 (DC8 profiles) and Figure 5 (P3 profiles) to facilitate a side-by-side comparison. For example, show O3 in the upper left corner in both Figures, and leave a panel blank if a given species isn't monitored by one of the platforms. I also recommend showing only the lines representing the means to improve readability. Many of the points overlap, and the variability represented by the individual points is hardly discussed in the text at any rate. If a discussion of the variability is considered necessary, consider showing extra panels depicting vertical profiles of the standard deviations for each species and mechanism.

Response: We thank the reviewer for these suggestions. Figures 3, 4 and 5 have been redrawn and only means are shown in the figures. Figure 5 has been reordered with common layout of Figure 3. Since the species measured by P3 and DC-8 are different as shown in Figures 3, 4 and 5, the layouts of Figures 5 and 3 cannot be combined to save space. On the other hand, when we try to combine Figures 3 and 4 together, we find that this will make the figure too crowded and too small because we will have to have 12 plots in one page. Therefore, we still keep Figure 4 in the revised manuscript.

Page 22,966, line 3: SAPRC-99 has the lowest NMB for SO2 based on P3 measurements, not CB05

Response: We agree with the reviewer. SO2 has been removed in the revised manuscript.

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Page 22,966, lines 1-3: please also list the species for which SAPRC-99 has the lowest NMB based on the P3 measurements, not just the species where CB4 and CB05 have the lowest NMB.

Response: OK. “SAPRC-99 has the relatively better performance for SO2” has been added in the revised manuscript.

Page 22,966, lines 3-4: The statement “in general, CB05 and SAPRC-99 yield similar results for different species” is not consistent with the results shown in Table 3 for the P3 flights. There are a number of instances where CB4 and CB05 are similar to each other but different from SAPRC-99 (e.g. NOy, NOz, PAN) and others where SAPRC-99 is closer to CB4 than CB05 (e.g. CO, NO2, isoprene, terpenes) Page 22966, line 14: should this be Figures 3 and 5, not Figures 3 and 4? The DC-8 NO and NO2 results are shown in Figure 5

Response: We agree with the reviewer. “in general, CB05 and SAPRC-99 yield similar results for different species” has been deleted and Figure 6 has been used in the revised manuscript.

Page 22,966, line 15: suggest inserting “likely” before “due”

Response: Done.

Page 22,966, line 18: Please insert “the” at the beginning of the sentence

Response: Done.

Page 22,966, line 22. Please remove the comma after “H2O2”.

Response: Done.

Page 22,966, line 23 – Page 22967, line 9: Most of this paragraph is dedicated to the discussion of model performance for a single species despite the fact that 8 species are shown in Table 3 and Figure 5. More discussion is needed for the other species. Also, given that the model performance for some of the species common to both the

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DC-8 and P3 flights varies between the two datasets, the slightly better performance for H<sub>2</sub>O<sub>2</sub> for CB05 relative to SAPRC should not be overemphasized both here and in the abstract and conclusions.

Response: We agree with the reviewer. This paragraph is mostly dedicated to the discussion of model performance for H<sub>2</sub>O<sub>2</sub> because we feel that H<sub>2</sub>O<sub>2</sub> is one of most important species that affect aerosol sulfate productions. Therefore, we want to have more discussion about H<sub>2</sub>O<sub>2</sub>. To address the reviewer's concern about the results of other species, we also add some more discussions about other species as follows "In addition, Table 3 shows that on the basis of DC-8 observations, CB4 has relatively better performance for O<sub>3</sub>, whereas CB05 has the relatively better performance for HNO<sub>3</sub> and SO<sub>2</sub>, and SAPRC-99 has the relatively better performance for HCHO and NO".

Page 22,967, lines 10 – 29: why is the discussion shifting back to the P3 results that were already discussed on page 22966?

Response: Since the paragraph is dedicated to the discussion of VOC (terpene and isoprene) results which have not been discussed before, therefore we discussed discuss P3 results about the VOC here.

Page 22,967, line 30 – Page 22968, line 1: can the authors speculate on how the use of MEGAN instead of BEIS may have affected these results?

Response: Done. To address the reviewer's concern, "Although MEGAN and BEIS provide different estimates for isoprene and other biogenic VOCs, these estimates are within the range of measured values for isoprene. Since MEGAN has higher isoprene estimates and if the ozone production was VOC-limited, then MEGAN would increase ozone. If ozone production were NO<sub>x</sub>-limited, however, the differences in MEGAN and BEIS would have little impact on ozone" has been added the revised manuscript.

Page 22,968, line 10: the "where" between "west" and "are" seems to be out of place

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Response: Done. The new sentence "...the west and southwest that are significantly affected by anthropogenic sources from..." has been used in the revised manuscript.

Page 22,968, Section 3.3: It is very hard to distinguish the various datasets in Figure 6

Response: Yes, this is because data from different datasets are overlapped each other.

Page 22,968, lines 22-25: Would these differences in model performance imply a realistic specification of boundary conditions for O<sub>3</sub> and SO<sub>2</sub> but potential problems with the boundary conditions for CO?

Response: It is difficult to make such a statement. To answer this question, we need more detailed study.

Page 22,968, line 27: Which sources or processes may have caused higher NO and PAN concentrations in the continental/clean flows compared to the southwest/west flows?

Response: To address the reviewer's concern, the following sentences "Henderson et al. (2009) suggested several reasons for model over-prediction of PAN; possible reasons include the uncertainty in the reaction rate of per-acetic acid with hydroxyl radicals, over-estimation of acetone photolysis, the omission of PAN photolysis, and omission of hydroxyl reaction with PAN" have been added in the revised manuscript.

Page 22,969, line 3: suggest adding a statement that this similarity is consistent with the use of the same boundary conditions for all simulations

Response: Done. "This similarity is also consistent with the use of the same boundary conditions for all simulations." has been added in the revised manuscript.

Page 22,969, line 5: suggest adding "all" before "three"

Response: Done.

Page 22,969, lines 14-17: But the P3 results shown in Figure 4 and Table revealed a

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strong overestimation of isoprene below 300 m and no systematic over- or underestimation when considering measurements at all heights. Therefore, it is not clear from the results shown whether biogenic emissions of isoprene were underestimated.

Response: We agree with the reviewer. However, the results discussed here are for coast on the basis of ship data. To address the reviewer's concern, "on the basis of the ship observations" has been added in the revised manuscript.

Page 22,970, line 10: please remove the comma after "CS"

Response: Done.

Page 22,970, lines 11-15: Would it be useful to compare the MWO observations to model results from a higher layer to address this issue?

Response: No, this is because the model already considers the effect of topography and the inability of the model to capture the inherent sub-grid variability at this location causes this bias. We need increase the resolution of model.

Page 22,970, line 24: suggest replacing "of chemical transport models" with "of the chemical transport model" or "of the chemical transport component"

Response: Done.

Page 22,971, line 12: suggest replacing "somehow" with "somewhat"

Response: Done.

Page 22,971, lines 12-19: please see my earlier comments. If listing the species for which CB-05 has the best NMB, the same should be done for CB4 and SAPRC, and such a listing should also be provided for the P-3, DC-8, and ship results. Otherwise, the impression is created that some results are highlighted selectively to make CB-05 look good.

Response: We agree with the reviewer. To address the reviewer's comments, the

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following sentence "On the basis of DC-8 observations, CB4 has relatively better performance for O<sub>3</sub>, whereas CB05 has the relatively better performance for HNO<sub>3</sub> and SO<sub>2</sub>, and SAPRC-99 has the relatively better performance for HCHO and NO" has been added in the revised manuscript.

Page 22,971, lines 19-20: Yes, but the low NMB is the result of compensating errors. The profiles in Figure 4 showed that isoprene is overestimated near the ground and underestimated aloft.

Response: We agree with the reviewer. To address the reviewer's concern, the following new sentences have been used in the revised manuscript "The three mechanisms overestimated isoprene below 300 m but slightly underestimated isoprene above 300 m. The three mechanisms systematically underestimated the observed terpenes by more than a factor of 2 most of time."

Page 22,971, lines 26-27. This statement is not true for isoprene. Also, along the lines of my comment above, it might be worth stating that CB4 had the best NMB for most species in Table 4.

Response: We agree with the reviewer. The new sentence "Model performance during southwest/west polluted flow conditions was similar to that noted for aircraft measurements except isoprene" has been used in the revised manuscript.

Page 22,972, lines 5-7: Please define which criteria are used to judge "reasonable" performance. Also, as the authors point out, there are many other factors besides the chemical mechanisms that affect the performance of the three systems analyzed here and compensating errors might very well be present. Therefore, it would be more appropriate to refer to the performance as that of the overall modeling system, not of the chemical mechanisms.

Response: We agree with the reviewer. "...the overall performance of the model system can be considered to be reasonable with NMB less than 30% in general" has been

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used in the revised manuscript.

Page 22,972, lines 7-11: An analysis of hydrocarbon measurements from the PAMS network might provide further insights.

Response: We agree. We plan to conduct such analysis in the future.

Page 22,972, lines 12-16: These two sentences, especially the last one, are not supported by the results shown in this paper. This paper has not shown that the updated treatment of reactions in CB-05 based on chamber studies yields any systematic improvements when incorporated into a regional-scale air quality forecast model. In fact, based on the results of this study, one could argue that in the particular configuration of the air quality forecast model analyzed here, CB4 leads to superior ozone forecasts under most atmospheric conditions because it is much less biased for  $O_3 < 75$  ppb and only marginally more biased for  $O_3 > 75$  ppb. Any claim about the superiority of a given mechanism needs to be based on the results shown in the paper or it does not belong in the conclusions.

Response: We agree. To address the reviewer's concern, the following sentences "On the basis of this work, overall none of the mechanisms performs systematically better than the others. However, it is important and necessary that the older chemical mechanisms be revised periodically to be consistent with current scientific knowledge. The CB05 mechanism has more detailed treatment of both inorganic and organic reactions and more number of species according to the state-of-the-science than CB4." have been used in the revised manuscript.

Tables 1-2,6: Table 6 should be moved before Table 3

Response: Done.

Figure 1a and 1b should be switched, and Figure 2 should be moved between Figures 1a and 1b.

Response: Done.

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Figure 3: Some species are missing from the caption

Response: Done. "Figure 4. Comparison of means of vertical  $O_3$ , CO,  $NO_x$ , NO,  $NO_2$ ,  $HNO_3$ ,  $NO_y$  and  $NO_2+O_3$  for the P-3 observations and model predictions during 2004 ICARTT period" has been used in the revised manuscript.

Figure 3-5: The legends for some panels run outside the bounding box. I also recommend showing only the lines representing the means to improve readability. Many of the points overlap, and the variability represented by the individual points is hardly discussed in the text anyway. If a discussion of variability is considered necessary, consider showing extra panels depicting vertical profiles of the standard deviations for each species and mechanism.

Response: We agree. Only means have been shown in the revised new Figures as suggested by the reviewer.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22955, 2009.

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