Paper and Comments: **GMDD - AMORE-Isoprene v1.0: A new reduced mechanism for gas-phase isoprene oxidation (copernicus.org)**

We are grateful to the referees for their helpful comments, and for the opportunity to improve the manuscript based on their input. We have copied the reviewer comments below and we respond inline (in blue **with changes to the main documents** *italicized***)**

Reviewer 1

This study presents the development of a new reduced isoprene oxidation scheme for application in a large-scale atmospheric model, using a benchmark state-of-the-science full description of the isoprene chemistry as a starting point, utilising a novel graph-theory based approach. The mechanism is then optimised and evaluated against its benchmark and other reduced schemes specifically designed for use in US regulatory models as well as limited chamber data, in box models as well as being incorporated into the US EPA Community Multiscale Air Quality modelling system (CMAQ v5.3.3) and evaluated against NE US air quality data.

This interesting study highlights the process of transparently developing a hierarchy of chemical schemes traceable to a benchmark mechanism that reflects the state-of-the-science in chemical understanding (Kaduela et al., 2015, doi:10.1016/j. atmosenv.2015.10.031).

The authors demonstrate a directed graph path-based automated model reduction approach, going through the necessary steps needed to reduce complex atmospheric chemical mechanisms, such as that for isoprene degradation, including optimisation and evaluation. This approach is certainly one of the main ways forward that atmospheric chemists should be using for dynamically constructing chemical mechanisms for a range of applications.

Comment 1:

The motivation and application of this study are well founded and reasonably well executed. However, I am not clear on what the main focus of this work is. Is it to demonstrate the first steps in using graph theory in the development of reduced chemical mechanisms from benchmark descriptions of (atmospheric) chemistry, or is it the development of a new reduced isoprene scheme, optimised and evaluated for specific conditions for use in US regulatory models? It could be both, but the paper should then be split into two clear sections, focused on these two motivations.

For example, the graph theory method sections are really interesting and initially set the paper off as a description of a new method for reducing complex chemical mechanisms. This is great and it's clear that a lot of effort has gone into the approach. However, this is largely undone by the requirement for the manual steps outlined in sections 2.3.5 and 2.4. The changes made here are quite substantial (adding a handful of reactions to a mechanism with 22 reactions soon represents a high proportion of the total mechanism) and so this paper does not demonstrate a method for automated mechanism reduction but rather is aiming to show off a new isoprene mechanism, optimised for a certain specific range of conditions.

We are grateful for the reviewer's overall positive assessment of this work. Indeed, the centerpiece of the paper is the new reduced isoprene mechanism rather than the reduction method, as was reflected, for example, in the title of the manuscript. That said, we note that graph theory motivated the design of our algorithm, and the concepts we used carried over to our manual optimization steps as well, where giving each mechanistic pathway (sequences of connected species in the graph) unique outputs was crucial in optimizing the mechanism. As mentioned in the final paragraph, a more fully automated model reduction method, building from lessons learned in this study, is currently under development and will be presented in a subsequent paper. We have gone through the manuscript to further clarify and emphasize these points in the revised text.

Line 19: *"This work demonstrates a new highly reduced isoprene mechanism and shows the potential value of automated model reduction for complex reaction systems."*

After line 85: *"The AMORE-Isoprene mechanism was the product of this methodology. Our novel algorithm was essential in the creation of this mechanism, but requires further work before it can be used for other mechanisms and without manual adjustment."*

After line 308 of revision (Section 2.4): *"The graph theoretical framework helped inform our decisions in this process. For example, the conceptualization of the mechanism as a set of unique pathways connected by sequences of reactions, which is rooted in graph theory, helped us to categorize reactions and how adjustments to their parameters would impact end results under different testing conditions."*

Also see the concluding paragraph (unchanged) of the paper (Lines 602-605):

"The AMORE-Isoprene mechanism demonstrates that there is significant potential advantage in the use of algorithms for model reduction. Additional development,

informed by the experiences of this study, is underway to more fully automate the model reduction process and further reduce the need for manual adjustments. Future work will extend this work to application to reduction of a wide range of atmospheric chemical mechanisms in addition to the isoprene oxidation mechanism."

Comment 2:

With this in mind, it feels like the validation/evaluation of the mechanism in section 3 focuses quite heavily on comparison to other mechanisms rather than comparison to measured data (whether from limited chamber experiments or ambient measurements). Again, if this were a paper displaying a mechanism reduction technique then it would be reasonable to make comparisons only to the mechanism you have reduced, but since there have been extensive manual changes to form the mechanism, this seems like more of an exercise to produce a good isoprene mechanism, in which case comparison to real-world data is required.

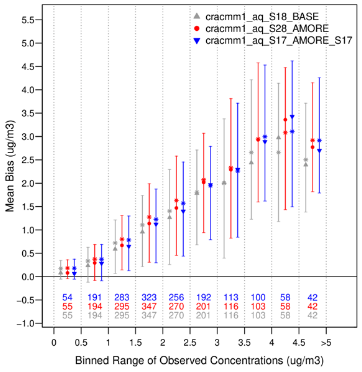
We agree that comparison to experimental and field data is important for model validation. This is why the model results were compared to chamber data in the context of the box model testing (e.g., section 3.2 and Figure 7) and to ambient data after implementation into CMAQ (section 3.3 and Figure 8). In the interest of brevity, not all testing results were shown in the original manuscript. To expand on what was shared in the original manuscript, additional binned bias plots similar to those in Figure 8 (in the original manuscript, now Figure 9 in the revision) for NOy, OC, and Isoprene have been added to the supplement Section 16.

This added Supplement section is shown here for ease of reference:

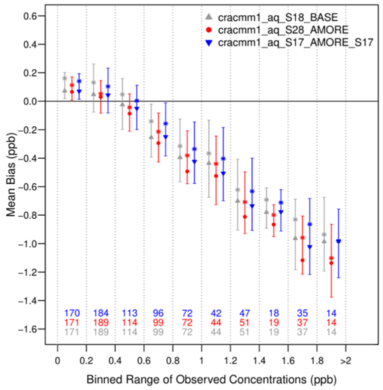
"Additional CMAQ results are shown in figure S.12. These plots show the binned bias of the AMORE mechanism for different ranges of the measured value. All measurements are part of the LISTOS campaign. The AMORE mechanism (red) is shown in comparison to the CRACMM1 base mechanism (gray) and a prior version of the AMORE mechanism (blue).

The AMORE mechanism shows slightly very slightly increased OC concentrations and slightly decreased isoprene concentrations, however the difference is not significant. There is no discernible difference in the NOy concentrations between the three mechanisms. Due to issues with the CMAQ run boundary conditions, the overall magnitude of the bias is confounded by many factors unrelated to isoprene. Thus, the *main conclusion to be drawn from these graphs is that the overall changes for these species is low."*

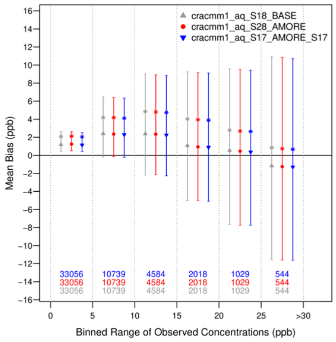
AMORE mechanism evaluation: OC biases



AMORE mechanism evaluation: Isoprene biases



AMORE mechanism evaluation: NOy biases



Based on the reviewer comments, we also concluded that more validation of the expanded Caltech mechanism we used as a basis for the model reduction would be helpful to put the paper and mechanism intercomparisons on a stronger footing. For more information on this please see the response to Comment 6, below.

Comment 3:

I also do not think that it has been demonstrated how well this mechanism performs under different atmospheric conditions for applications in other regional models. The input parameters used in the pathway importance algorithm and the model scenarios outlined in Table 2 and Table 3 do not demonstrate an ability to work in high-NOx environments. The High-NO_x case included is 5 ppbv. How would this mechanism work, for example, in urban conditions in China (where ozone titration of NO effects the NO/NO2 ratio as the day progresses) or even modelling atmospheric chemistry over the Bornean rain forest?

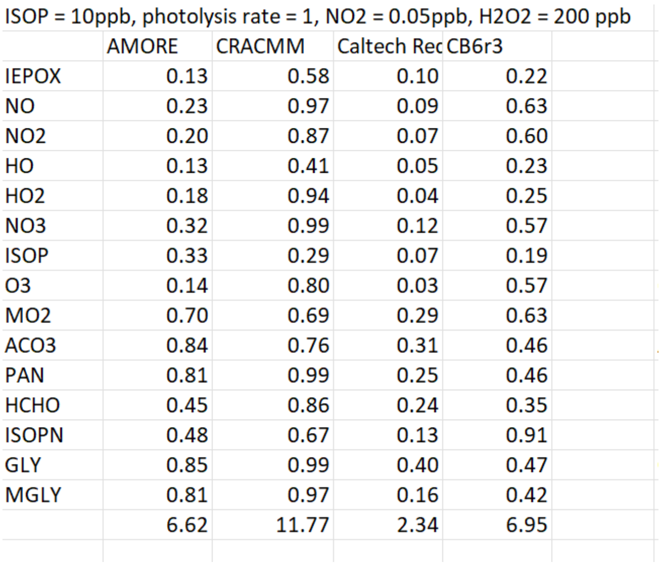
Based on the comments of both reviewers, we have investigated an expanded range of conditions (including elevated values for NO, NO_2, and OH) both for assessing the performance of AMORE Isoprene 1.0 and for assessing the sensitivity of the AMORE algorithm. Performance of AMORE Isoprene 1.0 is comparable or better than other small isoprene mechanisms, giving us confidence that this mechanism is suitable for low and high NO_x (and high ozone) scenarios. The added supplement section, S.15, is given here for reference and further discussion:

"S.15. Additional AMORE Box Model Simulations

Only six testing conditions were shown in the box model testing for the AMORE-Isoprene mechanism. Here we include additional box model results at more extreme conditions that are not well represented in the six main testing conditions. From these additional tests, we conclude that the AMORE-Isoprene mechanism is suitable for these additional extreme conditions.

The first additional testing condition was with very low NO_x concentrations. The initial NO_2 concentration was set to 0.05 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2, OH, and ozone are provided as well. At low NO_x, the AMORE-Isoprene mechanism continues to have low error for OH, NO_x, O_3, and other important species. As demonstrated by the Figure S.9, the AMORE is the most accurate small mechanism in these conditions.

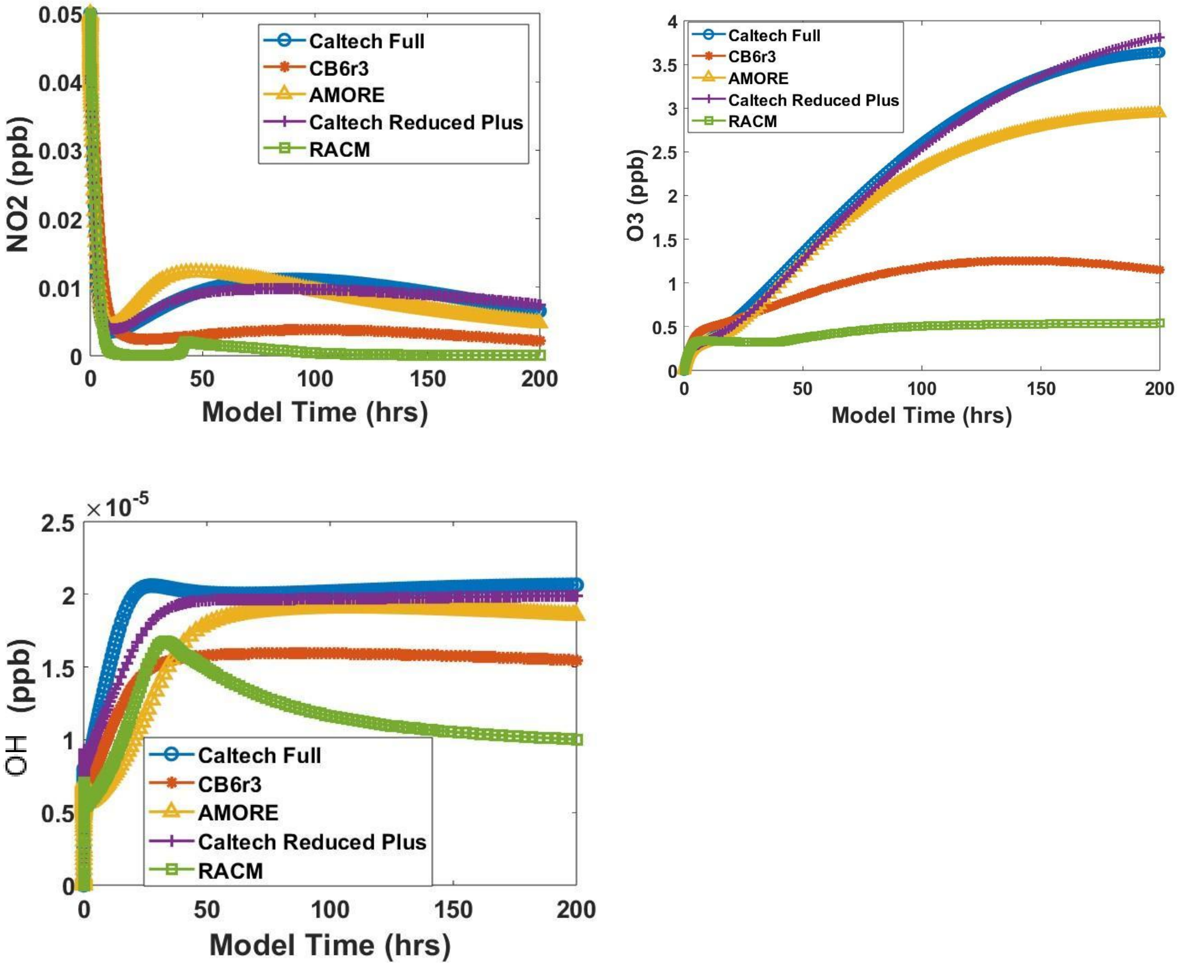
Table S.7 Very low NO_x error table



ISOP = 10ppb, photolysis rate = 1, NO2 = 0.05ppb, H2O2 = 200 ppb

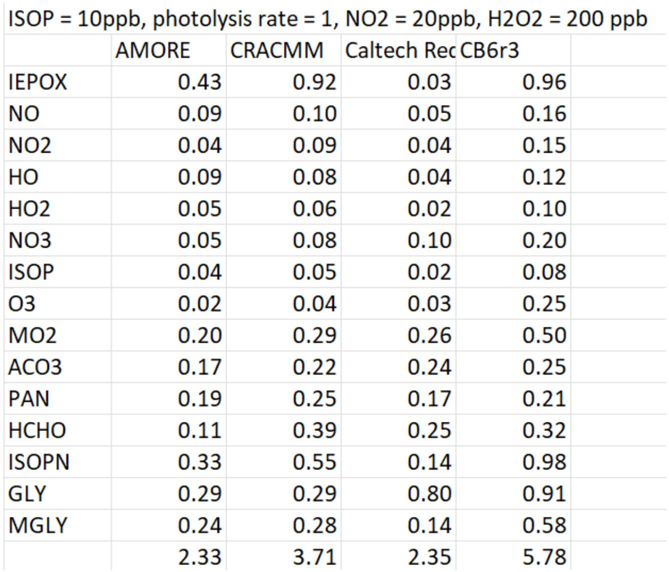
	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.13	0.58	0.10	0.22
NO	0.23	0.97	0.09	0.63
NO2	0.20	0.87	0.07	0.60
HO	0.13	0.41	0.05	0.23
HO2	0.18	0.94	0.04	0.25
NO3	0.32	0.99	0.12	0.57
ISOP	0.33	0.29	0.07	0.19
O3	0.14	0.80	0.03	0.57
MO2	0.70	0.69	0.29	0.63
ACO3	0.84	0.76	0.31	0.46
PAN	0.81	0.99	0.25	0.46
HCHO	0.45	0.86	0.24	0.35
ISOPN	0.48	0.67	0.13	0.91
GLY	0.85	0.99	0.40	0.47
MGLY	0.81	0.97	0.16	0.42
	6.62	11.77	2.34	6.95

Figure S.9 Very low NO_x (0.05 ppb) simulation, NO_2, OH, and O_3 Plots



The second additional testing condition was with very high NO_x concentrations. The initial NO_2 concentration was set to 20 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2 and ozone are provided as well. The results show that AMORE has strong agreement with the Caltech full mechanism for both ozone, NO_2, and many other species (see error table). This suggests that the AMORE isoprene mechanism is suitable for high NO_x conditions.

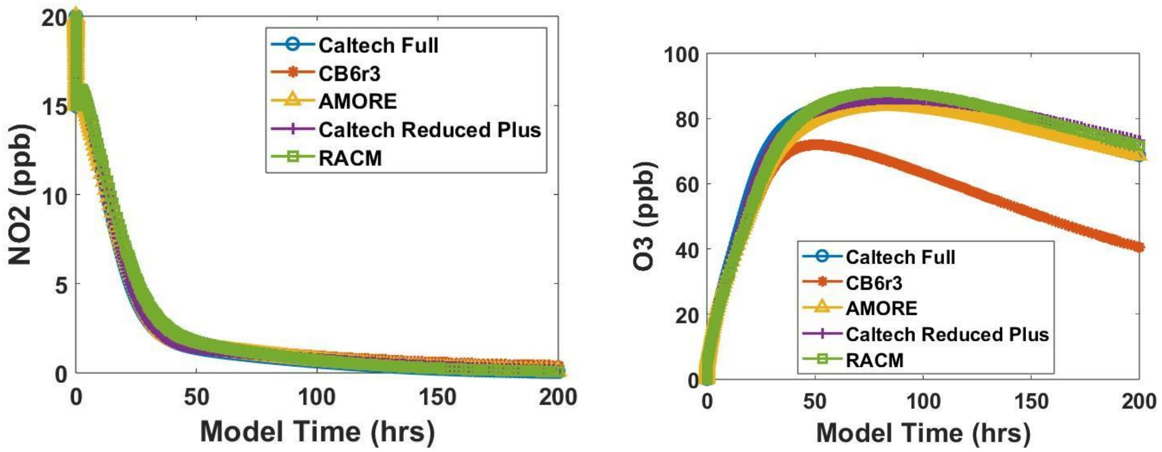
Table S.8. Very high NO_x error table



ISOP = 10ppb, photolysis rate = 1, NO2 = 20ppb, H2O2 = 200 ppb

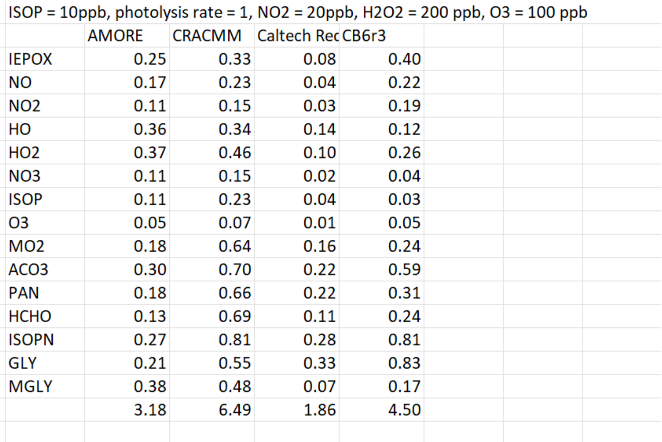
	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.43	0.92	0.03	0.96
NO	0.09	0.10	0.05	0.16
NO2	0.04	0.09	0.04	0.15
HO	0.09	0.08	0.04	0.12
HO2	0.05	0.06	0.02	0.10
NO3	0.05	0.08	0.10	0.20
ISOP	0.04	0.05	0.02	0.08
O3	0.02	0.04	0.03	0.25
MO2	0.20	0.29	0.26	0.50
ACO3	0.17	0.22	0.24	0.25
PAN	0.19	0.25	0.17	0.21
HCHO	0.11	0.39	0.25	0.32
ISOPN	0.33	0.55	0.14	0.98
GLY	0.29	0.29	0.80	0.91
MGLY	0.24	0.28	0.14	0.58
	2.33	3.71	2.35	5.78

Figure S.10 Very high NO_x (20 ppb) simulation, NO_2 and O_3 Plots



The final additional testing condition was with very high NO_x concentrations and high ozone concentrations. The initial NO_2 concentration was set to 20 ppb and the initial ozone concentration was set to 100 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2, OH, and ozone are provided as well. At high ozone and NO_x, the AMORE mechanism shows strong agreement for both ozone, NO_2, and OH concentrations (Figure S.10), and low error for most species (Table S.9). This suggests that the AMORE mechanism is suitable for high NO_x and high Ozone conditions.

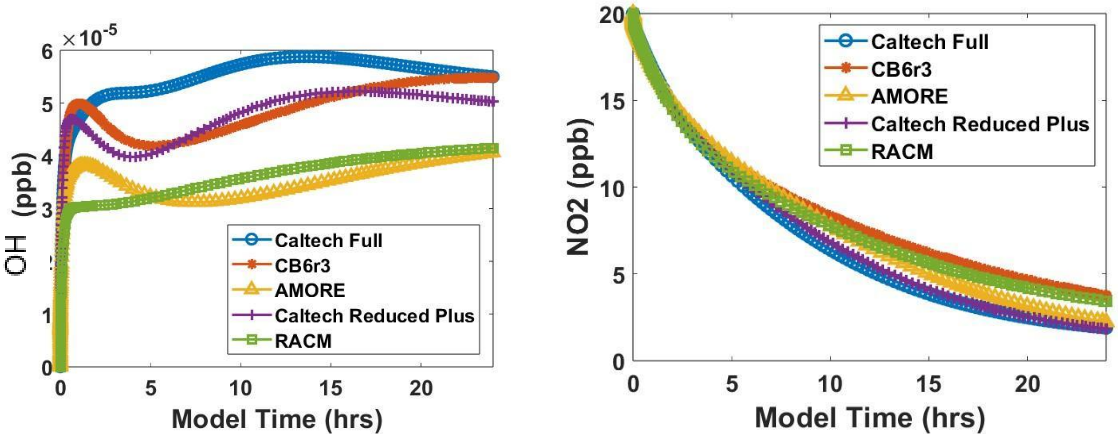
Table S.9 Very high NO_x and high ozone error table

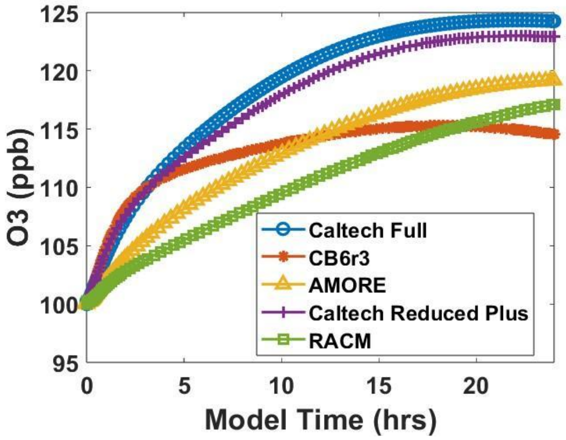


ISOP = 10ppb, photolysis rate = 1, NO2 = 20ppb, H2O2 = 200 ppb, O3 = 100 ppb

	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.25	0.33	0.08	0.40
NO	0.17	0.23	0.04	0.22
NO2	0.11	0.15	0.03	0.19
HO	0.36	0.34	0.14	0.12
HO2	0.37	0.46	0.10	0.26
NO3	0.11	0.15	0.02	0.04
ISOP	0.11	0.23	0.04	0.03
O3	0.05	0.07	0.01	0.05
MO2	0.18	0.64	0.16	0.24
ACO3	0.30	0.70	0.22	0.59
PAN	0.18	0.66	0.22	0.31
HCHO	0.13	0.69	0.11	0.24
ISOPN	0.27	0.81	0.28	0.81
GLY	0.21	0.55	0.33	0.83
MGLY	0.38	0.48	0.07	0.17
	3.18	6.49	1.86	4.50

Figure S.11 Very high NO_x (20 ppb) and high ozone (100 ppb) simulation, NO_2, OH, and O_3 Plots





”

The AMORE algorithm was somewhat sensitive to the range of conditions applied, in that some pathways were flagged as being significant at higher NO_x values and higher OH values that were not in the base parameter space. This suggests that it may be possible to identify an optimal mechanism for a special application such as modeling a highly polluted urban environment. However, the box model testing at high and low NO_x conditions indicates that these additional pathways are not necessary to maintain an acceptable level of accuracy. This test can be found in Section S.13 and Table S.5, and is referenced in Section 2.3.2.

For reference, the added supplement section is given here:

“13. Effects of Changing inputs on Pathway Importance Algorithm

The mechanism developed in Table S.5. The header column describes the changes made to the elevated value inputs to the algorithm. There were seven paths that remained unchanged for all inputs. These include {sol}, {O_3}, {NO_3}, {NO_3, sol}, {OH}, {NO}, and {OH, NO}. All other paths listed were only present in some versions of the inputs. For example, the path {NO, NO_2, NO_3} was only present when NO_2 concentrations were elevated to 5 ppb. When OH concentrations were elevated to 10^{-3} ppb (1 ppt, ~2.46 x 10^7 mol/cm^3), the overall number of OH paths decreased. This is likely because OH overshadowed other complementary species, causing their importance to be reduced while the {OH} path increased. All other changes are shown in the table.

Table S.5 Green indicates included path, red indicates unincluded path.

Pathway	Default values	NO = 5 ppb, NO_2 = 2 ppb	NO = 5 ppb, NO_2 = 5 ppb	OH = 10^{-3} ppb
{sol}	🟩	🟩	🟩	🟩
{O_3}	🟩	🟩	🟩	🟩
{NO_3}	🟩	🟩	🟩	🟩
{NO_3, sol}	🟩	🟩	🟩	🟩
{NO_3, HO_2}	🟥	🟥	🟥	🟩
{NO_3, HO_2, sol}	🟩	🟩	🟩	🟩
{NO}	🟩	🟩	🟩	🟩
{NO, NO_3}	🟩	🟥	🟥	🟩
{OH}	🟩	🟩	🟩	🟩
{OH, HO_2}	🟩	🟩	🟩	🟥
{OH, NO_3}	🟩	🟩	🟩	🟥
{OH, NO_3, sol}	🟩	🟩	🟩	🟥
{OH, NO}	🟩	🟩	🟩	🟩
{OH, NO, NO_3}	🟩	🟥	🟥	🟥
{NO, NO_2, NO_3}	🟥	🟥	🟩	🟥
{NO, HO_2}	🟥	🟥	🟥	🟩

Default values:

OH (ppb) = [10^{-6},10^{-4}],
NO (ppb) = [1.17×10^{-6},5.32×10^{-1}]
NO_2 (ppb) = [1.01×10^{-4},1.01×10^{-2}],
NO_3 (ppb) = [2.3×10^{-4},2×10^{-2}],
HO_2 (ppb) = [4.15×10^{-2},0.5],
O_3 (ppb) = [16.7,100],
CH3OO (ppb) = [0.1,0.2],
Sol (unitless) = 0.,1]”

Having said this, this work is certainly of great interest to the atmospheric science community and does indeed show a potentially interesting way forward for the future development of reduced chemical mechanisms. The work is therefore ideally suited for publication in GMD. I would recommended publication after the above and following comments have been considered by the authors.

Thank you for your positive evaluation of the manuscript and your helpful comments.

Specific Comments

Comment 4:

Table 1. The authors have chosen to compare the new scheme against those included in mechanisms primarily designed and optimised for use in US Regulatory models (except for the benchmark MCM and CalTech mechanisms). Why have you not also included comparisons to the Common Representative Intermediate (CRI) mechanism (CRIv2.2; https://doi.org/10.1016/j.atmosenv.2019.05.055)? This is a reduced scheme developed from the MCM (using a different lumping approach) for use in the EMEP MSC-W chemistry-transport model.

The CRI has been included in table 1. Thank you for this suggestion.

Comment 5:

L40: CRI should also be mentioned (and referenced) as a further example of a “lumped” approach.

CRI has been mentioned and the reference has been added to this line. Here is the updated line:

“The reduced models, including the Common Representative Intermediates mechanism, Regional Atmospheric Chemistry mechanism, and Carbon Bond mechanism have been developed manually by expert air quality scientists using techniques such as surrogate mechanisms (lumped structure (Yarwood et al. (2005)) or lumped species (Aumont et al. (2005); Goliff et al. (2013); Jenkin et al. (2019))), and empirical parameterization, along with expert knowledge of the reaction system.”

Comment 6:

L85 “Full Mechanism Input”: There are no files included in the supplementary giving the “full” mechanism, as described. It would be useful to give some examples of the extended/”missing” chemistry needed in the supplementary material.

“We have done some preliminary testing of this mechanism in comparison to experimental data, but it was difficult to attain meaningful results. Thus, further assessment of this updated mechanism is required” This is a worrying statement. What are the issues in obtaining “meaningful results? The integrity of the reduced mechanism depends on the benchmark “full” description of the chemistry, and so testing and evaluation of this scheme is a key step in the process and needs to be evaluated/shown.

We agree that more clarity is needed in the text regarding the testing we had done previously. First, we note that full information regarding the extended mechanism had been provided in the code and data repository (https://github.com/fcw2110/AMORE_supplementary_files), as cited in the “Code availability” section of the original manuscript, but to increase the visibility of this important information it is now also listed in the Supplement section S.18 and the key modifications to the Wennberg et al. 2018 mechanism are described and italicized.

The Wennberg et al. 2018 Caltech mechanism and its reduced versions have been validated previously by their authors, and the Reduced Mini version is the default isoprene mechanism for GEOS-Chem v. 14.02 (Wennberg et al. 2018, Bates and Jacob 2019). As we mentioned in Section 2.1 of the original manuscript, the approach we used in creating the expanded Full mechanism emulated the process that the Caltech group used when creating their Caltech Reduced Plus and Caltech Reduced Mini mechanisms starting from the Caltech full mechanism. The ‘Plus’ represents added degradation reactions for all species. They had not previously added degradation reactions to their full mechanism, so it was necessary to make this update before using their full mechanism as an input to our reduction algorithm.

The extended base mechanism was tested in the F0AM box model framework and compared to the Wennberg 2018 mechanism, against Caltech chamber data and EUROCHAMP chamber data. Performance between the two “full” mechanisms was very similar for early generation oxidation products since that part of the mechanism was not altered. We make new reference to the EUROCHAMP comparison in the paper on line 98:

“Further details are available in supplement section S1 including box model comparisons of original and extended mechanisms to EUROCHAMP data (Muñoz (2021a), Muñoz (2021b)). In addition, the extended mechanism is listed in its entirety in supplement Section 18.”

The added discussion in the supplement section S.1 is given here for reference. The first section describes the differences between the extended and original Caltech full mechanism and shows box model results, and the second section discusses comparisons to EUROCHAMP data:

"The Caltech full Isoprene mechanism (Bates and Wennberg 2018) was updated for this work. The original mechanism did not contain complete oxidation pathways for all of the species present in the mechanism. The reasoning behind this was that several species did not have published or known oxidation schemes. Since this mechanism was not designed for use in 3D models, the incomplete chemistry was not an issue.

However, for this work, complete chemistry was needed, as we were attempting to utilize the accuracy of the full mechanism for the reduction process. To do so, we needed to update the full mechanism to contain oxidation pathways for all species. Most of the work for this process was already done by Bates et al. in the preparation of their reduced plus isoprene scheme. However, they completed oxidation pathways only after lumping many multifunctional isoprene species together. They used SAR and existing mechanisms (MCM) to complete the chemistry for these species.

We utilized the information from their reduced plus isoprene scheme to create a complete full mechanism. To do so, we first created a correspondence between lumped species in the reduced plus mechanism and species in the full mechanism without an oxidation pathway. From there, the reactions of the lumped species were replicated for the un-lumped species. If a lumped species was a reactant, then a new reaction was created for each species that it represented. If a lumped species was a product, then the reaction coefficient was divided evenly into the represented species set, thus conserving carbon flux between the two mechanisms.

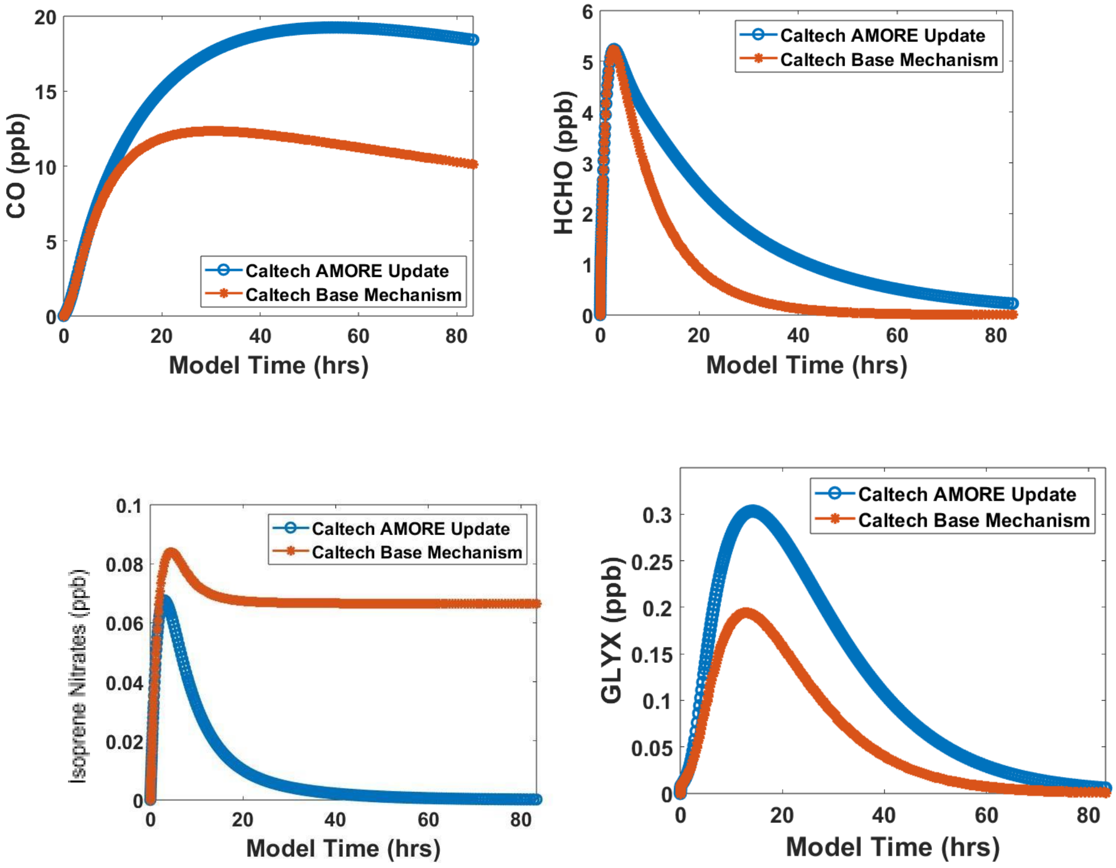
In addition to incomplete isoprene chemistry, the Caltech full mechanism did not complete oxidation pathways for species considered outside of the isoprene scheme. The oxidation chemistry for these additional species was taken from the MCM scheme.

The updated Caltech full isoprene mechanism is ideal for box model simulations for the purpose of mechanism reduction, as it can be considered more accurate for dynamic oxidant concentrations and common oxidation products such as formaldehyde and carbon monoxide.

All of the changes made to the mechanism at this stage were additive. No reactions were removed from the mechanism. Compared to the original mechanism, the degradation of highly oxidized isoprene derived species increases the production of carbon monoxide, formaldehyde, glyoxal, and methylglyoxal. The most significant change is in carbon monoxide production over long run times. These changes also reduce the overall concentration of oxidized isoprene species, such as isoprene nitrates, over long time frames. The plots below show the impact of the changes for a single simulation. Effects are similar for other simulation conditions.

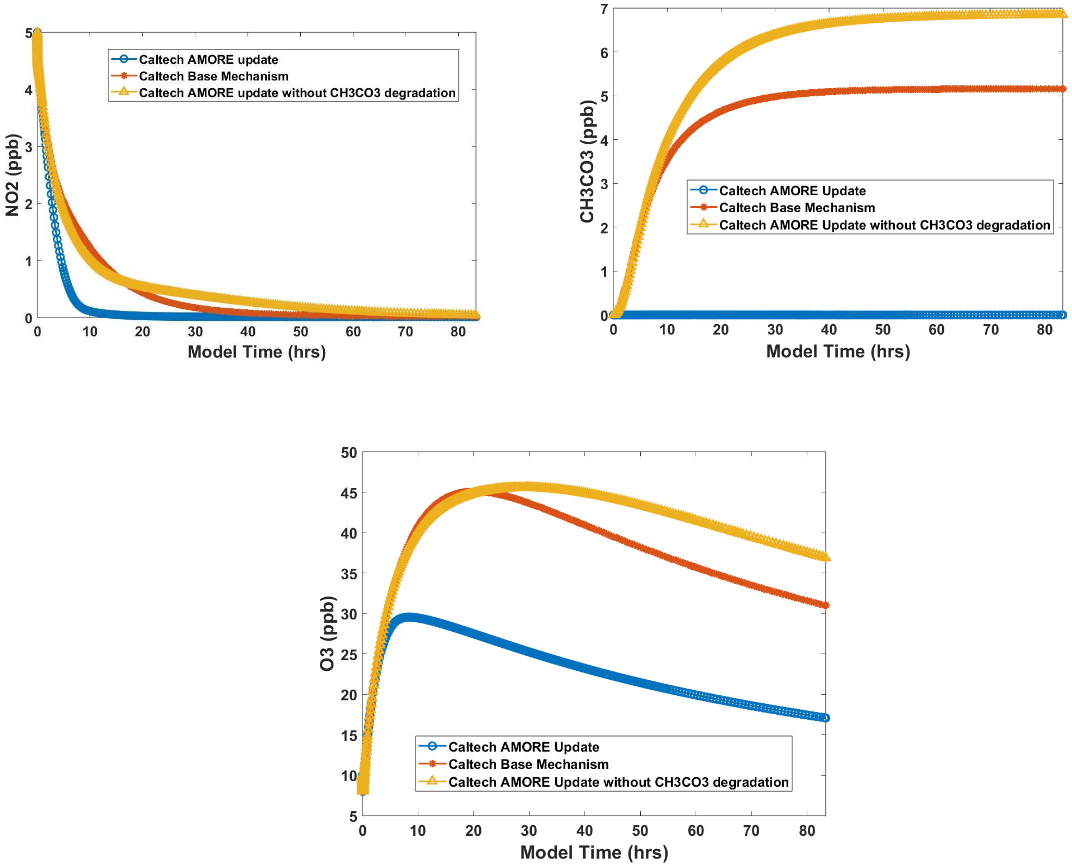
Figure S.1

Simulation settings: 200 ppb H2O2, sza/photo constant = 1, NO_2 = 0.2 ppb, ISOP = 10 ppb



The changes to the degradation of small molecules had a significant effect on nitrogen radical cycling. In particular, the addition of degradation pathways for the $CH3CO_3$ radical had a major effect on NO_2 cycling and ozone production. The impact of this particular addition is shown in the plots below, wherein the base caltech mechanism, updated caltech mechanism, and updated mechanism without $CH3CO_3$ degradation are shown.

Figure S.2 *Simulation settings: 200 ppb H2O2, sza/photo constant = 1, NO_2 = 5 ppb, ISOP = 10 ppb*



As shown in the graphs, the degradation of $CH3CO_3$ leads to a significant reduction in NO_2 concentrations, and therefore a reduction in ozone concentrations.

The Caltech full isoprene mechanism was used as the basis for the Caltech Reduced mini mechanism, which has become one of the default mechanisms for the GEOSChem 3D model and has undergone validation by its authors (Bates and Jacob, 2019). The

Caltech reduced mini mechanism is still 108 species and therefore a more highly reduced version could be useful for large-scale modeling. It is important to note that the extensions of the oxidation chemistry we made to the baseline Caltech mechanism are analogous to the extensions made by the Caltech group prior to reduction when they created the Caltech reduced plus and Caltech reduced mini mechanisms.

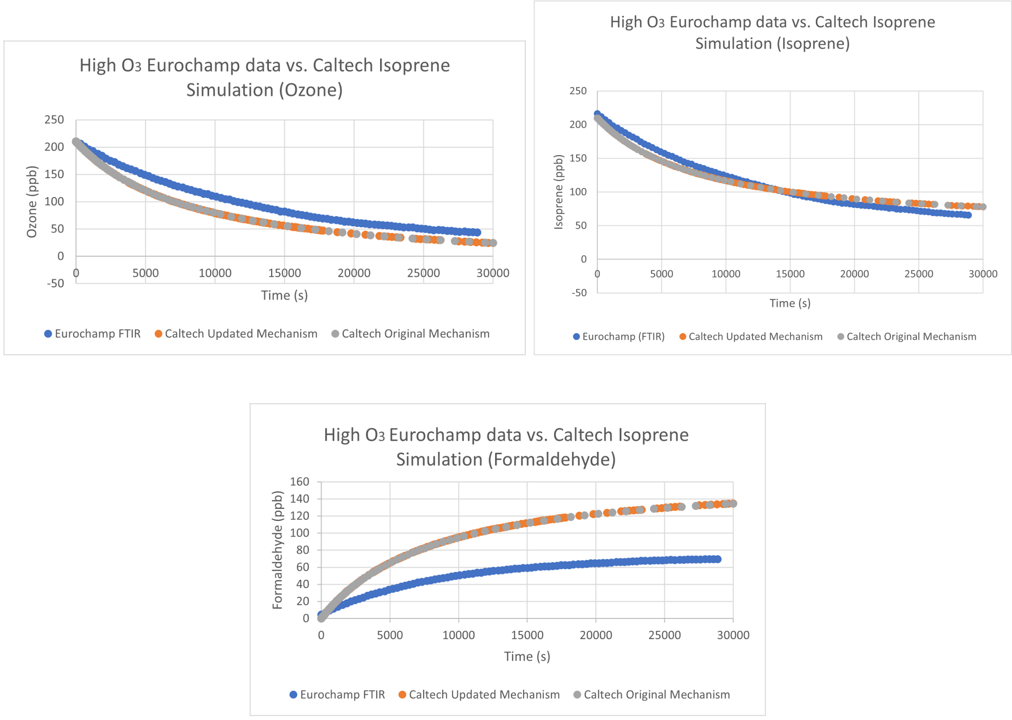
Most experimental datasets, including the Paulot data discussed in section 3.2 and shown in in Figure 8 (9 in revision) as well as data found in the EUROCHAMP and FIXCIT databases, do not effectively enable an intercomparison between the Caltech full mechanism and our extended Caltech base mechanism. This is because no changes were made to the first three generations of isoprene chemistry or the IEPOX chemistry, and the species these experimental studies tracked were mostly confined to that part of the mechanism. Therefore, agreement with, e.g., the Paulot et al. IEPOX chamber data shown in Figure 8 (9 in revision) is the same for the Caltech Full and our extended mechanism. The main impacts of the extended oxidation chemistry are on later-generation oxidation products, carbon monoxide, formaldehyde, ozone, and nitrogen radicals, that is, species which, for the most part, were not tracked in these experiments.

We used data from two EUROCHAMP experiments to compare the update to the Caltech baseline. The experiment with the most data for isoprene and stable operating conditions suitable for simulation was the high O_3 *experiment. This experiment, along with the high NO experiment, were the only ones identified that had simultaneous measurements of* NO_x*, isoprene, ozone, formaldehyde, and carbon monoxide. For the high NO experiment, the* NO_2 *concentrations reported in the data had multiple peaks and troughs, suggesting unreported loss and addition throughout the experiment, making it unsuitable for simulation. However, with some assumptions, reasonable agreement was observed between the two mechanisms and the reported MVK, isoprene, and formaldehyde data. The Caltech and the extended Caltech mechanisms performed similarly.*

For the high O_3 *experiment, agreement between the two mechanisms and measured ozone and isoprene was strong. Both mechanisms were biased high for formaldehyde compared to the experimental data, with similar accuracy.*

Figure S.3

Simulation Conditions, P = 1000 mbar, T = 295 K, ISOP = 210 ppb, O_3 = 210 ppb, H_2O_2 = 10 ppb, CO = 200000 ppb, NO_x = 0 ppb, Photolysis = 0



The main conclusion to be drawn from this comparison to EUROCHAMP data is that the Caltech Full and Caltech Full Extended mechanisms perform very similarly for these experimental conditions and the measured species. Comparison to future well-controlled chamber studies designed to characterize the final oxidation steps of the isoprene mechanism would better highlight the differences between the mechanisms."

Comment 7:

L109: "NO_x" is not an oxidant. Do you mean "NO3"? However, NO_x (i.e. NO and NO2) are key species in the radical propagation cycles (NO to NO2 conversion efficiencies are an important metric) and so should probably be included.

The terminology has been changed throughout the paper. The phrase "oxidants and nitrogen oxides" is now used to describe the following species : OH, HO_2, O_3, NO, NO_2, NO_3 and MO_2.

Comment 8:

L125: Include important representative references of the “many prior works”

The following references have been added:

“Many prior works have utilized graph theory to analyze chemical mechanisms (Ratkiewicz and Truong (2003) , Lu and Law (2005), Pepiot-Desjardins and Pitsch (2008), Sun et al.(2010), Nikolaou et al. (2018), Silva et al. (2021)).”

Comment 9:

Figure 2 (and within the text): In what respect is NO an “oxidant” here? NO is often stated as an oxidant in the text, which I don’t think it is (RO2 is the oxidising species). If you want/need to describe NO as an oxidant you need to define why.

This has been changed in the text. See response to comment 7 for more detail.

Comment 10:

L156: Which “oxidants” are held constant?

For clarity, the list of species held constant for running the algorithm has been given in parentheses in the text and the terminology has been changed from oxidants to oxidants and nitrogen oxides. (OH, HO_2, O_3, MO_2, NO, NO_2, NO_3).

The line now reads: *“The algorithm takes oxidant and nitrogen oxide concentrations (OH, HO_2, O_3, MO_2, NO, NO_2, NO_3, which are treated as constant…”*

Comment 11:

L189: A visualization of the yield estimation algorithm is not shown in Figure S.4.

It was provided as Figure S.4. on page 13 of the supplement, but, since the caption and figure were separated by a page break, perhaps the reviewer missed it. Due to new figures being added to the supplement, this figure is now figure S.8. Additional explanation accompanying the figure has been added.

Comment 12:

L196: Again, not comfortable with NO and NO_2 being described as “oxidants”.

The terminology has been adjusted. See response to comment 7 for more detail.

Comment 13:

Table 2 shows that the elevated NO and NO_2 conditions are very low. While I appreciate that the role of these elevated conditions is not to represent ambient conditions, setting these elevated values too low could result in pathways being deemed "not important" as the yields of species produced under really high NOx conditions (10s of ppbv) would not be given a chance to change from the baseline conditions. How is "solar intensity" defined?

As mentioned previously, the performance of the AMORE Isoprene 1.0 mechanism and the AMORE algorithm were both tested under an expanded range of conditions (see response to Comment 3 above).

Solar intensity is defined based on the input to the F0AM simulation. All photolysis functions are multiplied by the reported intensity, so a value of 0 indicates that no photolysis occurs. Most of the photolysis reactions in the Caltech mechanism have the form:

Reaction = 'MVK3OOH4OOH = MGLY + OH + OH + HCHO';

Rate constant = SUN.*3.0E-5;

In this case, the solar intensity is the SUN constant, so at a solar intensity of 1, the rate constant of this reaction would be 3×10^{-5} s^{-1}.

The following line has been added to section 2.4.1 (box model testing) for clarification:

"The rate of photolysis reactions are scaled by a unitless parameter labeled as hv. The value of this parameter was calibrated to match results of Paulot et al. (2009) chamber data for high photolysis conditions."

Comment 14:

L220: "Care was taken in the selection of inputs to balance breadth of input conditions with relevance to the atmosphere" Do the conditions outlined in Table 2 really cover the optimal range of atmospheric conditions?

The goal in selecting input conditions was to find values that were relatively low and relatively high without biasing the algorithm with extreme values. They do not represent the full range of values that each input takes. As noted in the response to Comment 3, the AMORE Isoprene 1.0 mechanism performs satisfactorily under more extreme conditions than those that were used as input conditions to the algorithm, but it would be possible to create a mechanism optimized for a more extreme scenario using the

AMORE algorithm. Section S.13 shows the sensitivity of the algorithm to a select set of differing inputs.

Comment 15:

Table 3 shows that all of the models start with 0 initial O3 except for the High O3 model. Given the effect of O3 on NOx partitioning, it seems that this could have quite an impact on NO concentrations in all of the models. It could be good to run at least a model with (properly) High NOx and high O3. Also in Table 3, I don't think it is specified what photolysis conditions the models are run under (or what low hv actually means, is it 0 photolysis?).

A simulation with high NO_x (NO_2 = 20 ppb (t = 0)) and high ozone (O_3 = 100 ppb (t = 0)) has been added to the supplementary error tables (Table S.6), and a discussion of the results has been added as well (Section S.14). In addition, simulation results with high NO_x (NO_2 = 20 ppb (t = 0)) and no change to ozone, and low NO_x (NO_2 = 50 ppt (t = 0)) have been included.

The performance of the AMORE mechanism is similar in these tests to its performance in other conditions, so the results have not been included in Table 6.

Table 3 specifies the photolysis constant for each condition in the row with hv in the species column. The low photolysis condition has a photolysis constant of 0.5 compared to 3.5 for other conditions, signifying that photolysis reactions are 7 times slower in the low photolysis condition.

Comment 16:

L371 and onwards describe the addition of IHN as a priority species, but outlines that this addition was done manually. Why was IHN not included as a priority species from the beginning? It seems like this could lead to some changes in the mechanism since IHN has formation routes from OH and NO3 but the current mechanism only includes formation from OH.

This species was initially omitted from the priority species list because it did not meet our criteria as an important species, described in section 2.2:

"Besides isoprene, these species were chosen for their importance for SOA or brown carbon formation and/or expected impact on gas-phase photochemistry (isoprene epoxydiols (lumped), isoprene nitrates (lumped), glyoxal, methylglyoxal, methacrolein, methyl vinyl ketone, peroxyacetyl nitrate, methyl radical, peroxyacetyl radical). Formaldehyde was also included in the protected species list due to its status as an air

toxic (EPA (2018); Zhu et al. (2017); Scheffe et al. (2016)) and for its potential to indicate oxidant levels (Travis et al. (2022)).”

Although some isomers of IHN have been suggested to undergo hydrolysis in aqueous aerosols (Vasquez et al. PNAS 2020), it is not a major source of SOA in the CMAQ model, and therefore it was not initially included in the priority species list. Subsequently, it was identified as having an important impact on gas-phase photochemistry during our 3D modeling in CMAQ and a manual adjustment to the mechanism was made. In future work IHN will be considered a priority species.

Comment 17:

L382: “Table 4”

The word “table” has been added.

Comment 18:

L392-3 states that "the {NO3, HO2, hv} pathway was determined to be unnecessary...". If this is the case, why wasn't it excluded by the pathway importance algorithm? What was the rationale behind removing this pathway and replacing it with those listed?

The removal of this pathway was a subjective decision based on the observation that it contributed relatively little to the improved performance of the mechanism. In adding other reactions, we determined that this was a pathway that could be removed without significant loss in accuracy. Had this paper been solely focused on demonstrating the algorithmic process, we would not have made this change, but there was also a driving goal to have a high-performing mechanism with as few reactions as possible.

Perhaps one reason why the pathway importance algorithm identified this pathway was that the algorithm gave high weighting to the scenario in which photolysis and NO_3 chemistry are dominant. However, NO_3 chemistry is more often dominant in dark conditions. Thus, if the algorithm was run without high photolysis and NO_3 concentrations as concurrent phenomena, then this path likely would not be chosen as important.

Comment 19:

Figure 3: “pbb” to “ppb”. Give reaction numbers which are adjusted. How do the comparisons highlighted in Figure 3 look for other conditions (NO)?

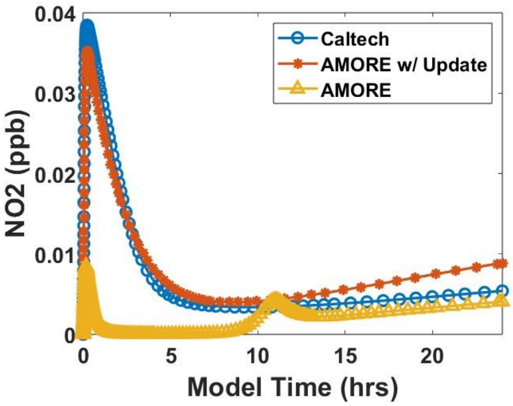
Thanks for pointing out the typo; it has been corrected.

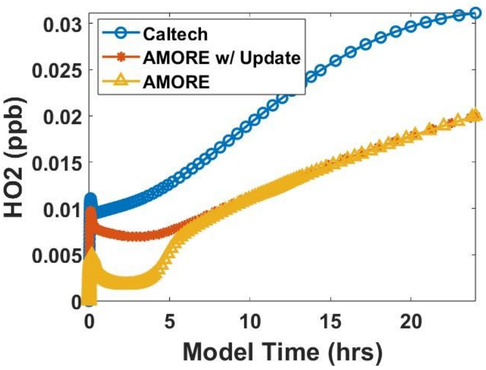
The Figure caption has been fixed to show the reaction numbers of the adjusted reactions. Here is the updated caption:

"Box model simulations (T = 292 K, p = 1000 hPa) showing the improvement in performance of the AMORE mechanism for HO2 and NO$_x$ after adding these species to the products of reactions 4 (b) and 5 (a)."

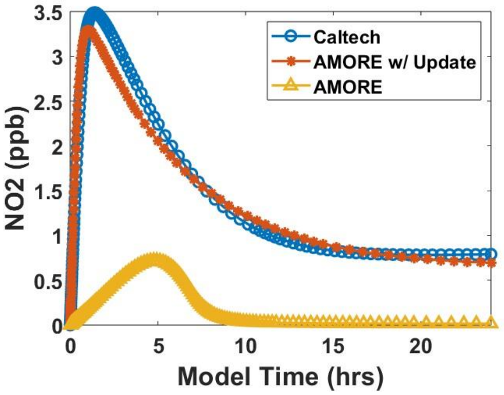
We ran the same comparison under lower and higher NO$_x$ conditions. For the ISOPOO + NO reaction shown in Figure 3.a), the improvement is consistent for all NO$_x$ concentrations. Below are plots under the same conditions except for changes to NO initial concentrations:

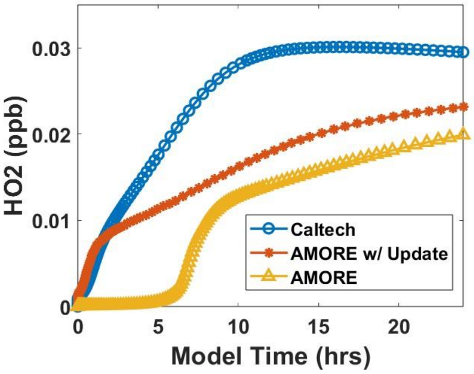
NO = 0.05 ppb



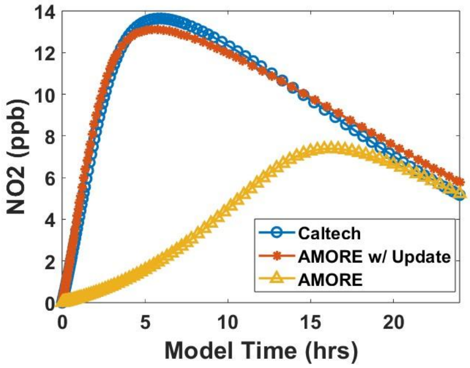


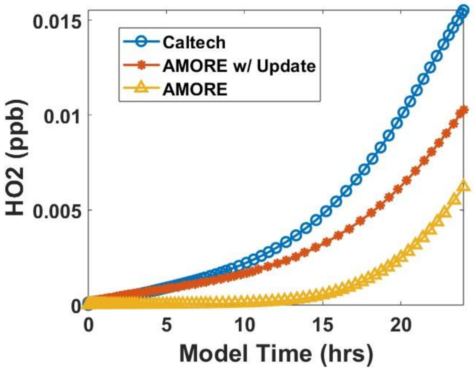
NO = 5 ppb





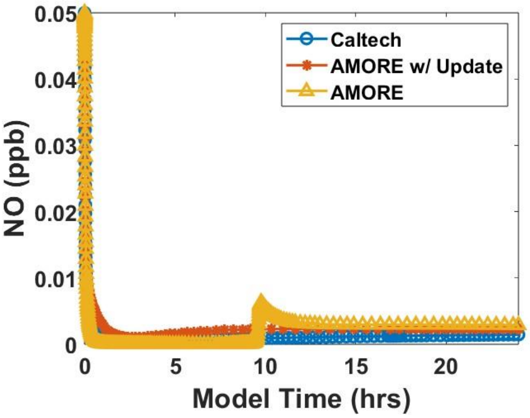
NO = 20 ppb

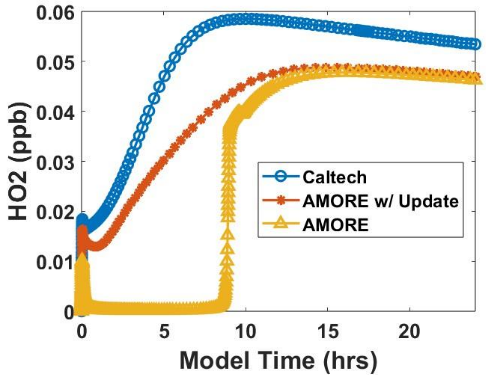




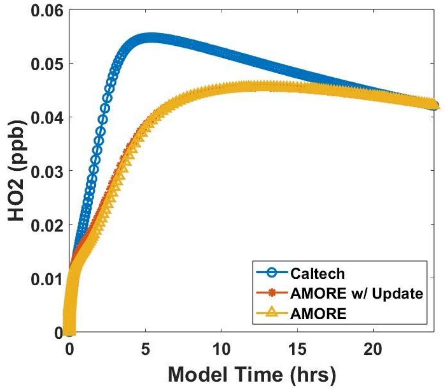
For the ISOPOO + HO2 reaction (figure 3.b), the improvement is only noticeable at lower NO concentrations, where that reaction is more prominent. At higher NO concentrations, the update has no effect. Below are plots under the same conditions except for changes to NO initial concentrations:

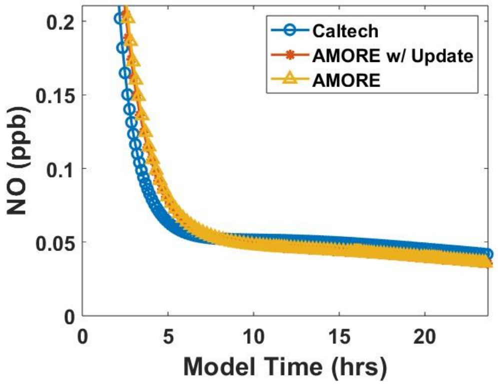
NO = 0.05 ppb





NO = 5 ppb





We now mention this extended testing in Section 2.4.3 and have included these plots in supplement section S.17.

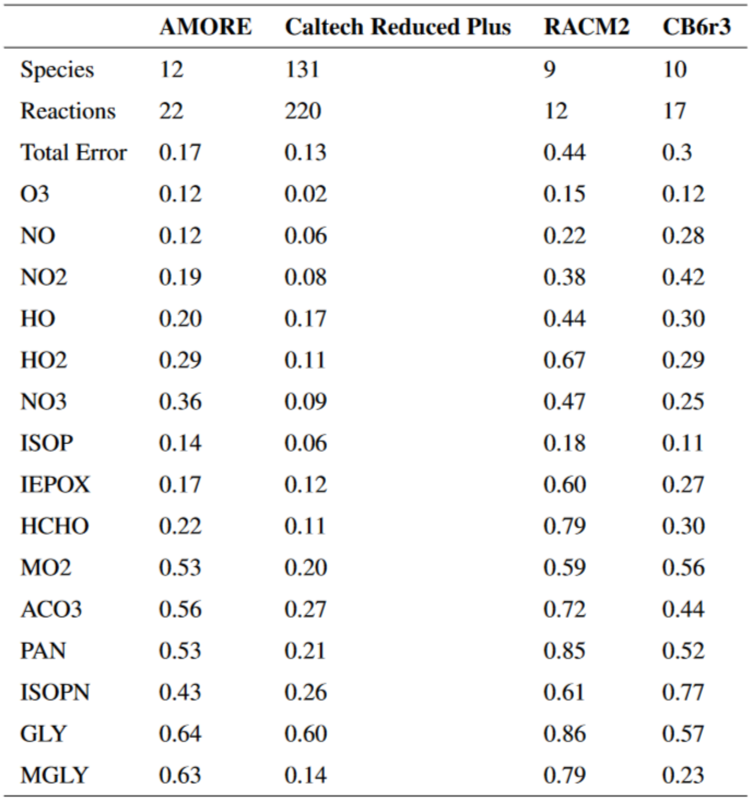
Comment 20:

Section 2.4.4 outlines the Total Error Metric. This metric seems quite arbitrary, particularly with regards to the weightings applied to each group (Table 5). To avoid issues with the decisions made around weightings for each species in the total error calculation, I would suggest that the error for each species should be presented in Table 6 (particularly since the specific error values are listed below for many of the species anyway). The total error could still be kept in Table 6, though I don't know how much use it is since different use cases would prioritise better predictions of different species/groups.

The individual species errors (averaged over the 6 conditions tested) have been added to Table 6.

The goal of the error metric was to be able to create a single value to describe the performance of a mechanism. This is particularly useful when comparing multiple different versions of an algorithmically generated mechanism, where the number of mechanisms makes comparing the results for each species impractical. Our choice of weighting is informed by our knowledge of the mechanism and modeling priorities and prior works (Bates and Jacob (2019)). We realize that a single weighting scheme will not apply equally well to all applications; the scheme we have proposed is relevant to those interested in modeling isoprene chemistry. Going forward, we believe that creating standardized metrics will be useful in comparing competing mechanisms, especially as new algorithmic methods for generating and reducing mechanisms are developed. We are opting to include the error metric results, as this demonstrates a way of creating a standardized metric.

For the purposes of this table, adding the individual species errors was straightforward and easy to interpret. Thank you for the suggestion. Here is the updated table for reference (Table 6):



	AMORE	Caltech Reduced Plus	RACM2	CB6r3
Species	12	131	9	10
Reactions	22	220	12	17
Total Error	0.17	0.13	0.44	0.3
O3	0.12	0.02	0.15	0.12
NO	0.12	0.06	0.22	0.28
NO2	0.19	0.08	0.38	0.42
HO	0.20	0.17	0.44	0.30
HO2	0.29	0.11	0.67	0.29
NO3	0.36	0.09	0.47	0.25
ISOP	0.14	0.06	0.18	0.11
IEPOX	0.17	0.12	0.60	0.27
HCHO	0.22	0.11	0.79	0.30
MO2	0.53	0.20	0.59	0.56
ACO3	0.56	0.27	0.72	0.44
PAN	0.53	0.21	0.85	0.52
ISOPN	0.43	0.26	0.61	0.77
GLY	0.64	0.60	0.86	0.57
MGLY	0.63	0.14	0.79	0.23

Comment 21:

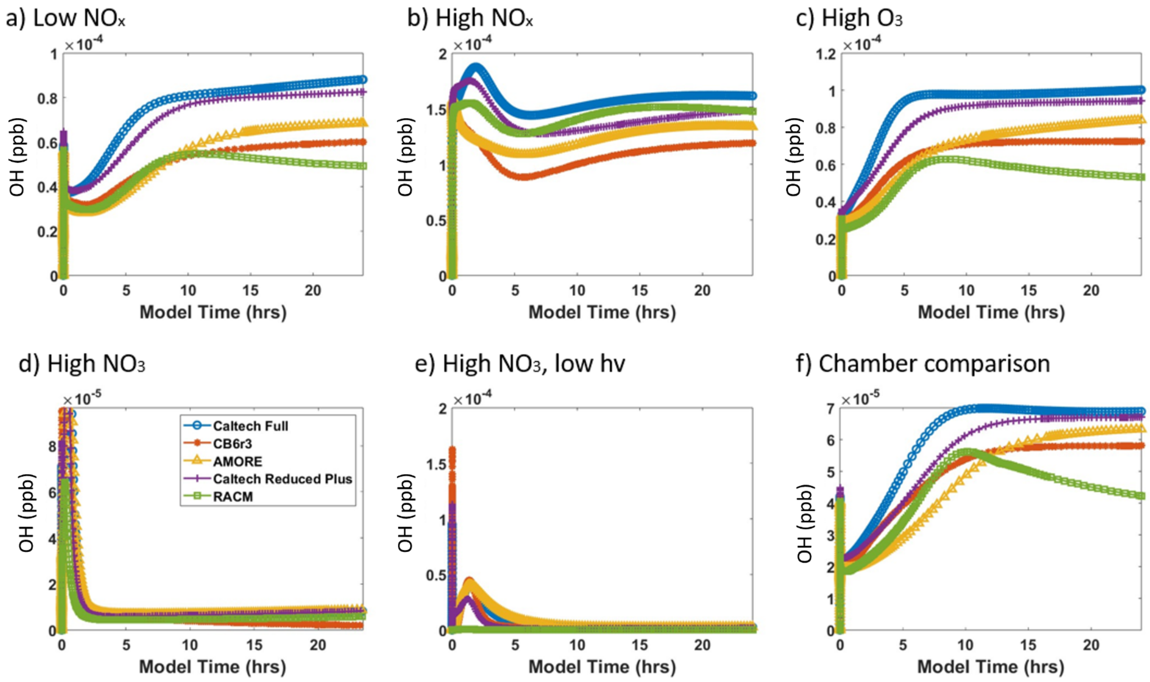
L446: Why not 5% for GLY?

The numbers were rounded so that they would cleanly add to 0.33 without too many digits. Starting with a SOA contribution of 2.5%, and adjusting for the species ignored (other tetrafunctionals and other species), glyoxal would be adjusted up to a total contribution of 3.8% of total SOA represented. However, it was boosted at the expense of the other two contributing categories since they already had a much larger weighting, and 4.5% of the SOA weighting led to a total weighting of 0.015, which had the benefit of few significant figures.

Comment 22:

L472: Why only show comparisons for HCHO and HO2? What about for other important AQ species? (O3, HOx, NOx, GLY/MGLY?)

We chose these two species because they exemplify the improvement from the AMORE mechanism and they added a visual element to the error numbers reported in Table 6. The other suggested species were omitted from the original manuscript in the interest of saving space. A figure for OH has been added (Figure 6):

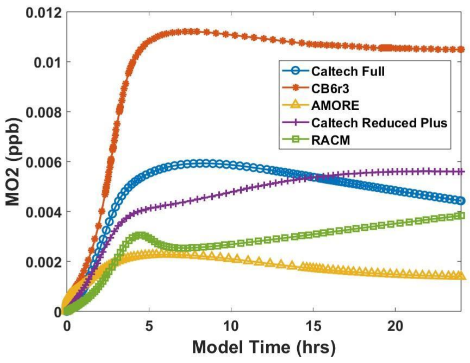


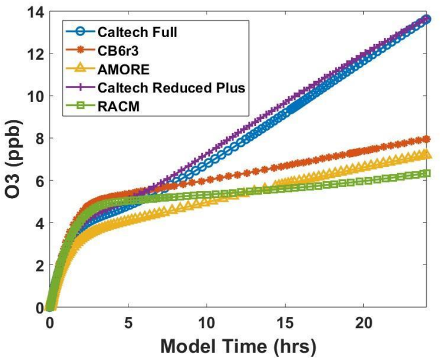
and plots for the rest have been added in the supplement (S.18):

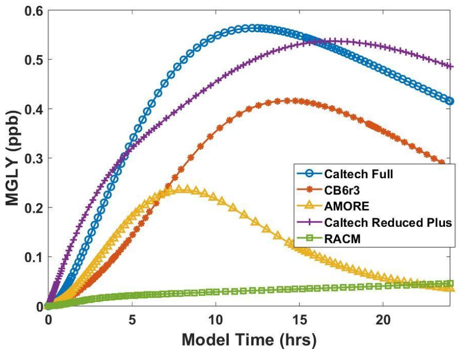
“S.18 Additional Box Model Plots

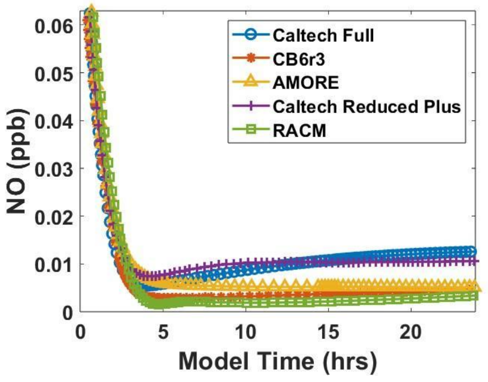
The following box model plots show additional species in the six primary conditions tested. The species included are isoprene, ozone, MGLY, GLY, MO2, ACO3 and NO.

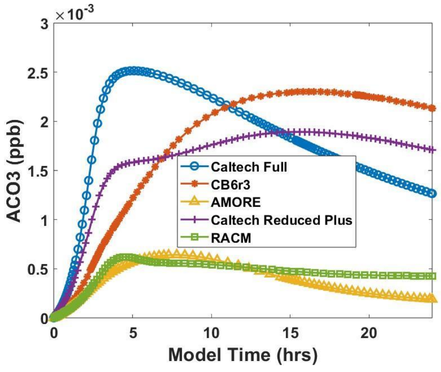
Figure S.15. Low NO$_x$

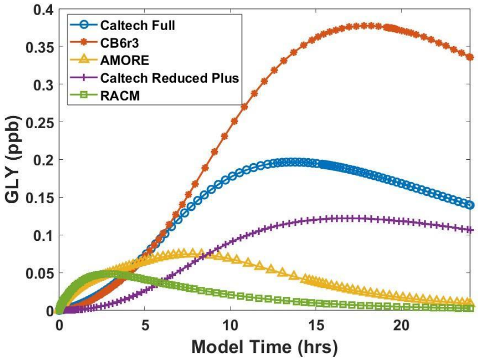

MO2 (ppb)
0.012
0.01
0.008
0.006
0.004
0.002
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


O3 (ppb)
14
12
10
8
6
4
2
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


MGLY (ppb)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


NO (ppb)
0.06
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


×10^-3
3
2.5
2
1.5
1
0.5
0
ACO3 (ppb)
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


GLY (ppb)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

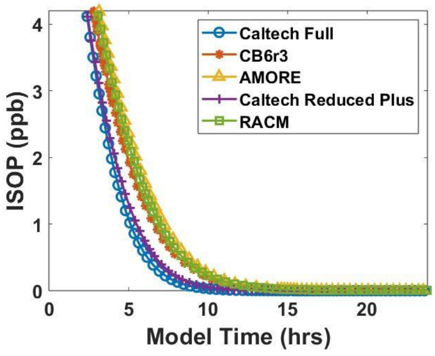
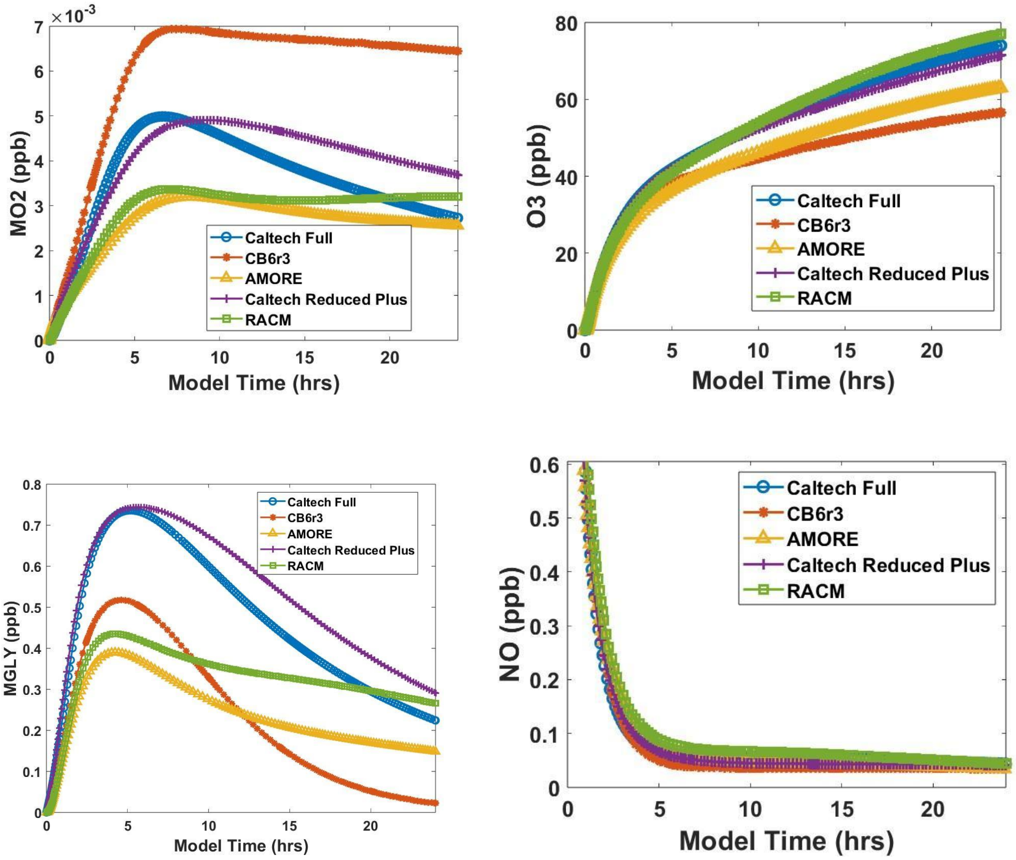

ISOP (ppb)
4
3
2
1
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

Figure S.16. High NO$_x$



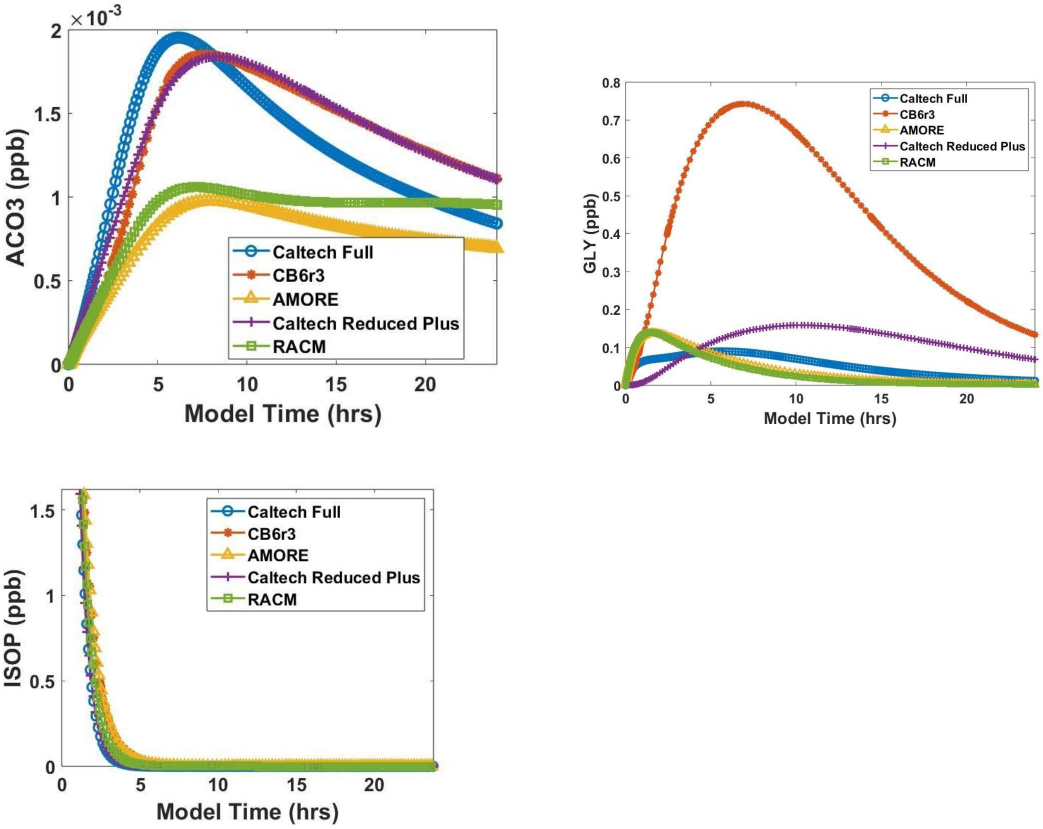
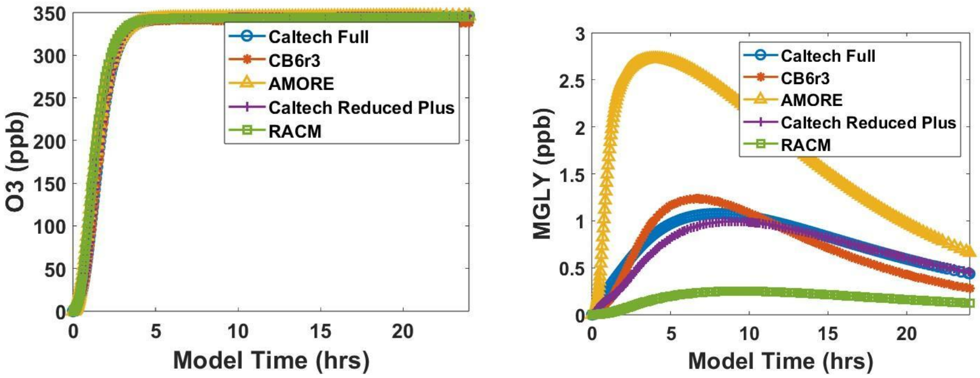
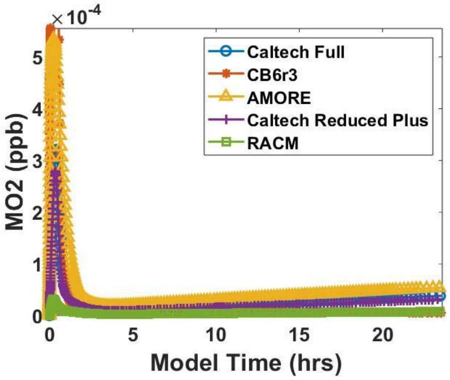
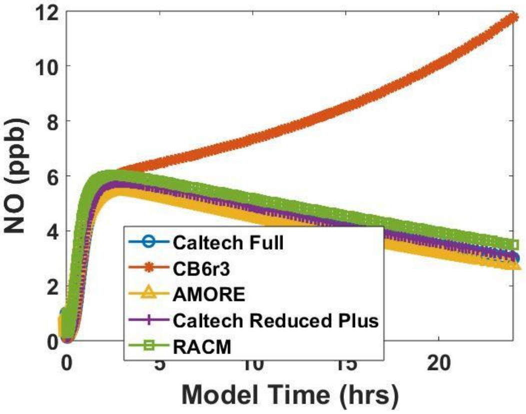
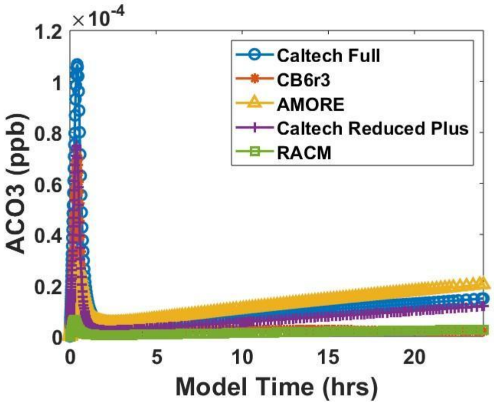


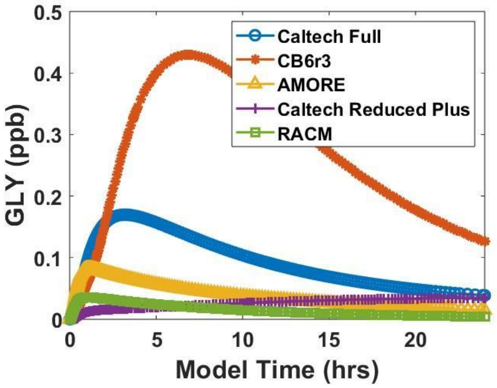
Figure S.17. High NO$_3$




×10⁻⁴
MO2 (ppb)
0
1
2
3
4
5
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


NO (ppb)
0
2
4
6
8
10
12
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


×10⁻⁴
ACO3 (ppb)
0
0.2
0.4
0.6
0.8
1
1.2
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


GLY (ppb)
0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

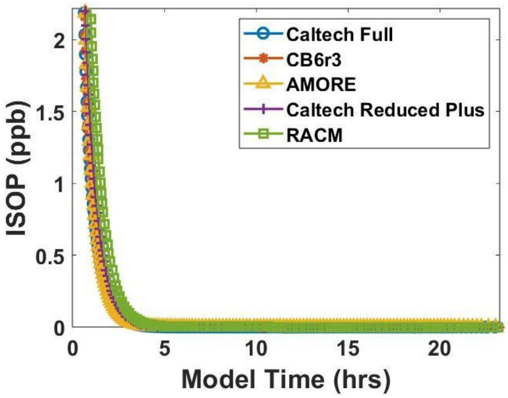
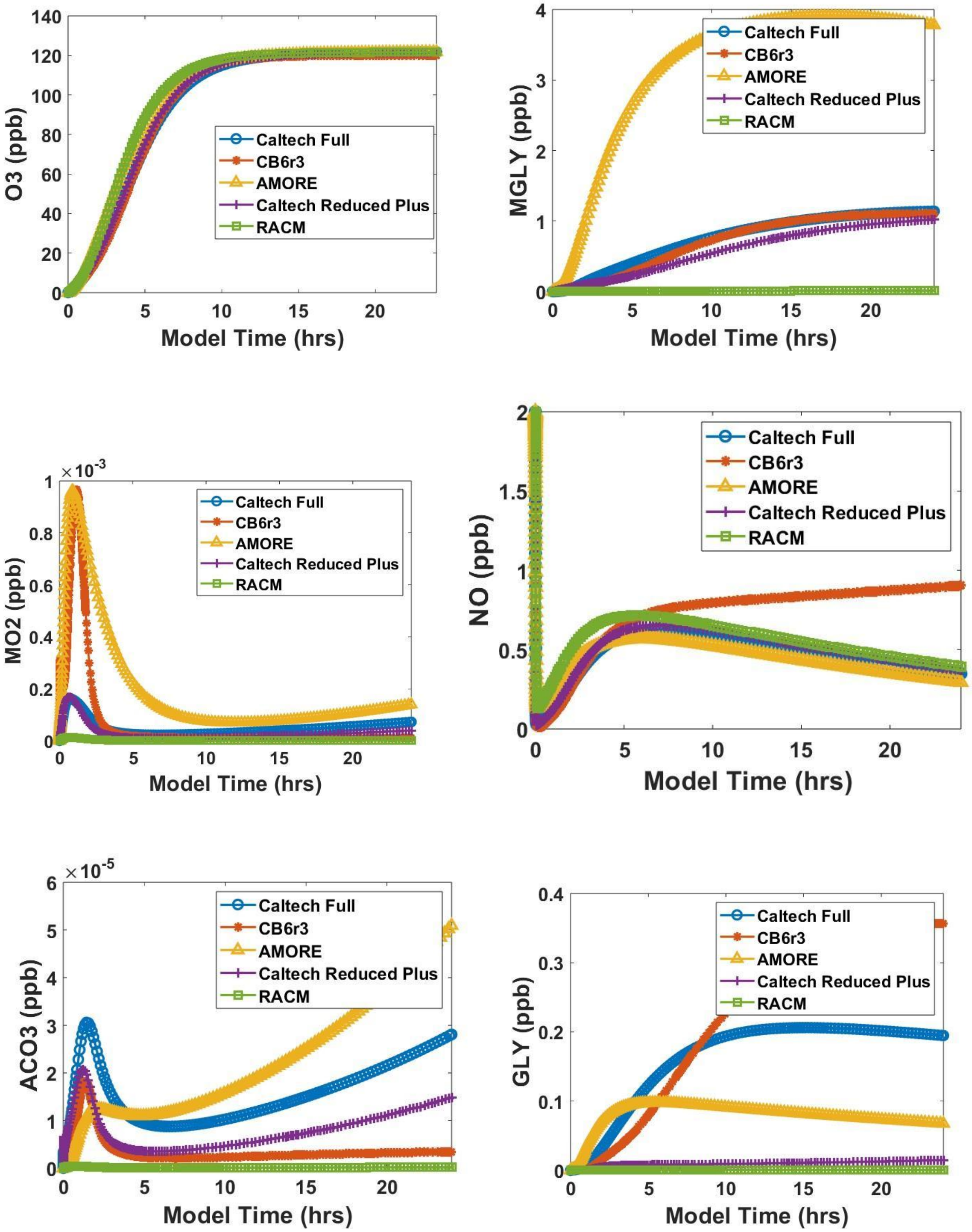

ISOP (ppb)
0
0.5
1
1.5
2
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

Figure S.18. High NO_3 low hv



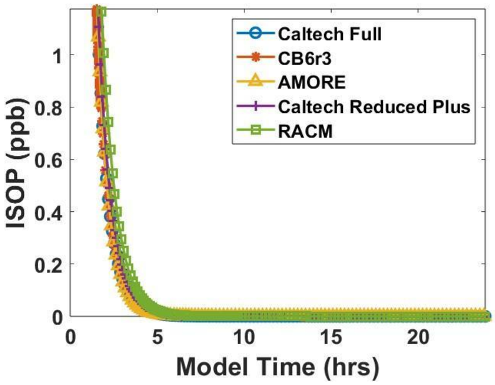
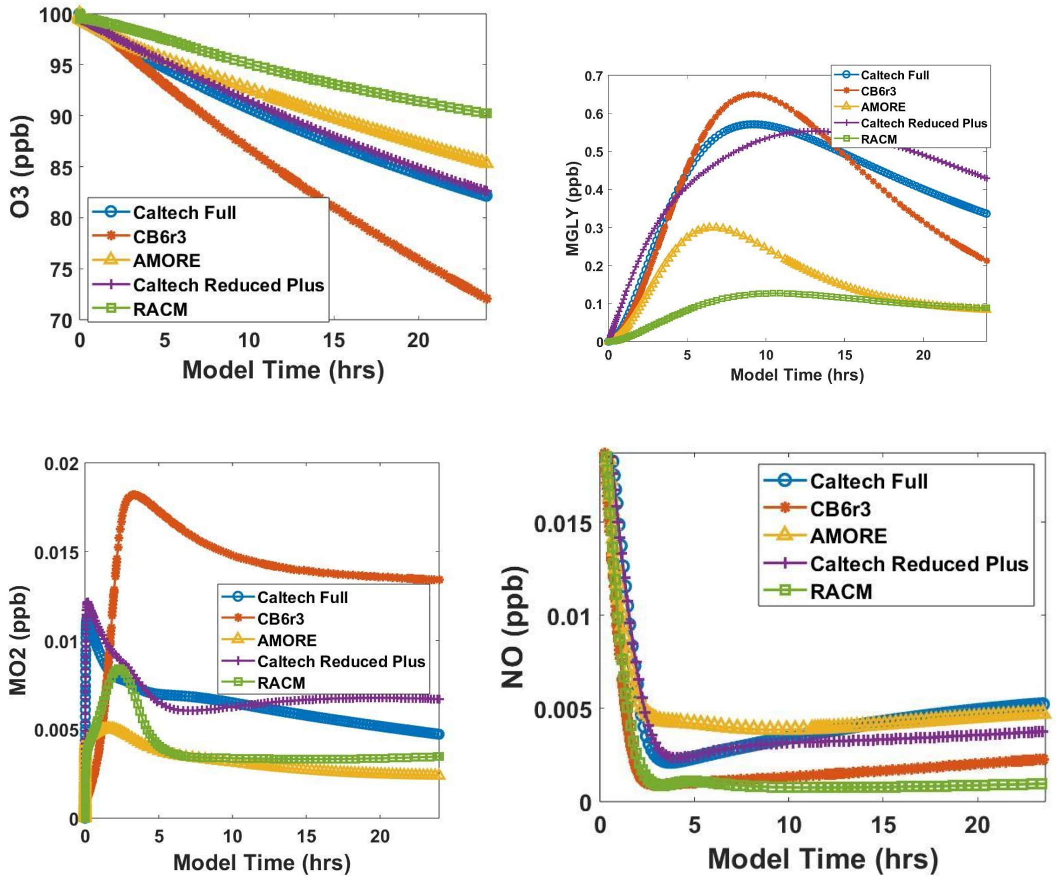
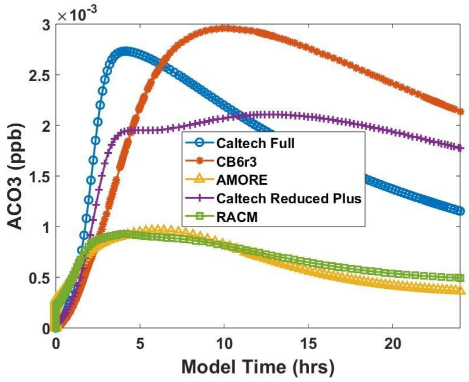
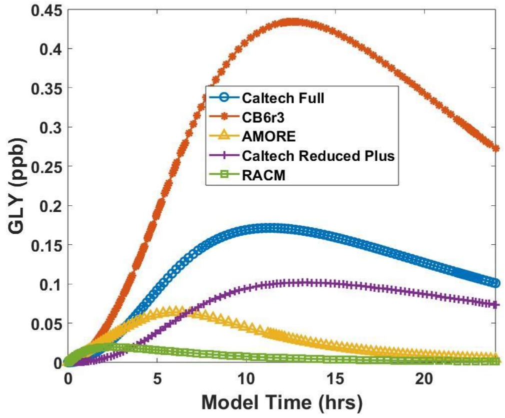


Figure S.19. High O_3







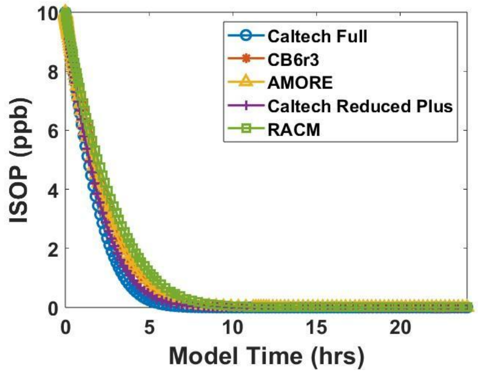
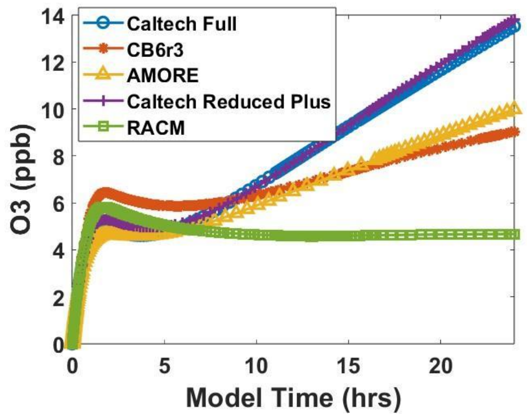
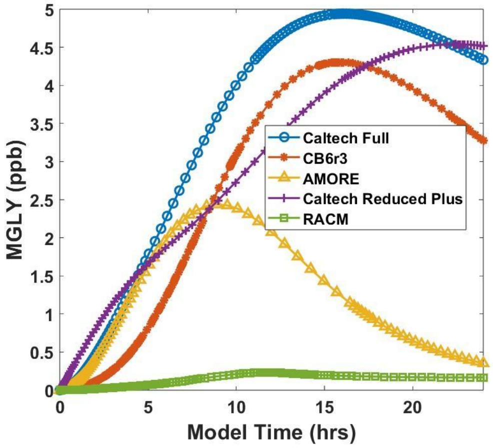
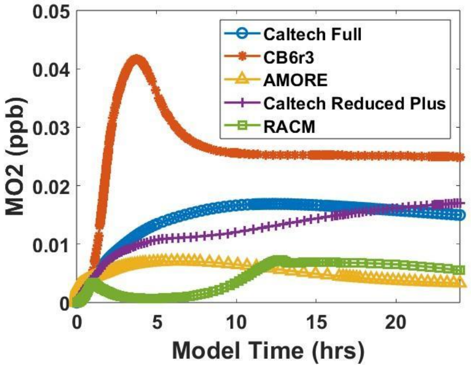
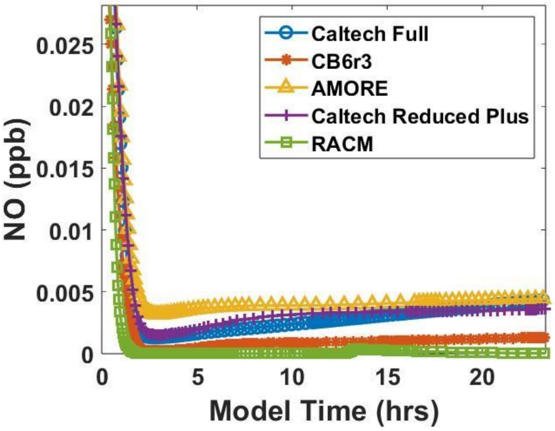


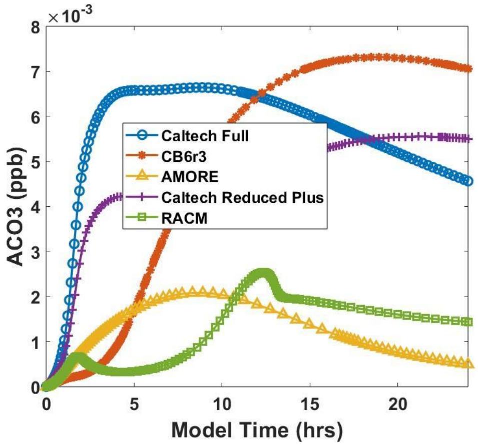
Figure S.20. Chamber Comparison

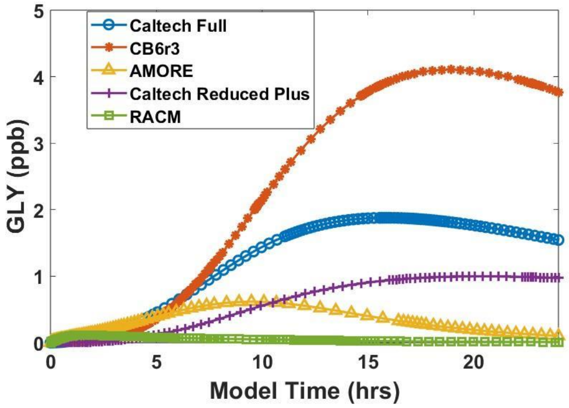


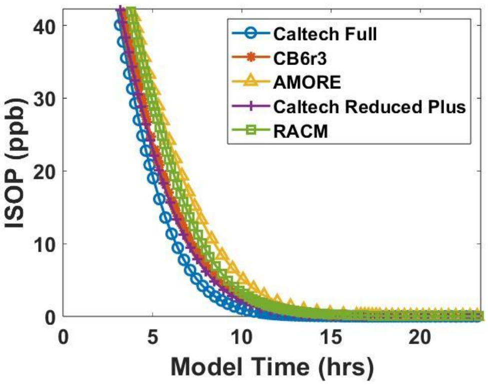












Comment 23:

L474 says "Figure 3.1" where it should say "Figure 4"

The figure number has been changed to 4.

Comment 24:

L507 says "shwon" instead of "shown"

The spelling has been corrected.

Comment 25:

Figures 4 and 5: Why was the box model not “spun-up” first to radical steady state conditions (then show comparisons for non-radical important AQ species)? Comparisons seem to show new mechanism doing a better job than RACM but not CB6…

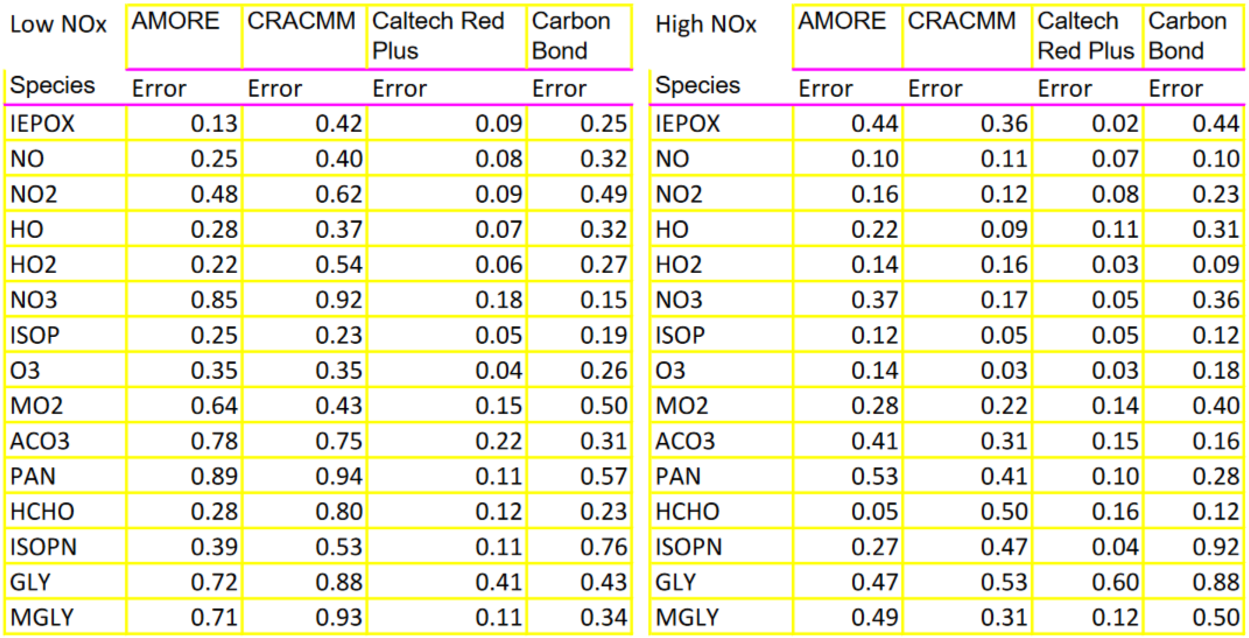
The simulation of dynamic conditions allowed for a demonstration of the performance of the mechanisms with regards to these radicals. The influence of isoprene chemistry on radical concentrations was a desired property to emulate, and non steady state conditions were the most suitable for this. These simulations were also suitable for intercomparison with chamber data.

Comment 26:

L515 should reference the table in the SI with a number. However, I can't actually find the full error tables for each mechanism in the supplementary.

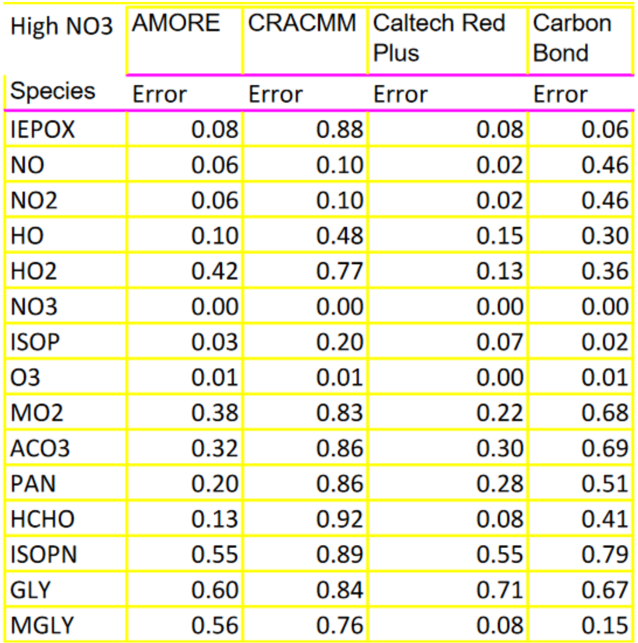
Our apologies for the confusion. The tables were not included in the written supplementary document, but were available as files in the supplementary file folder as described in the Code Availability section. We have now included the full error tables in the written supplement (S.15) for easier reference. Here are those tables:

Table S.6. Error tables for box model simulations

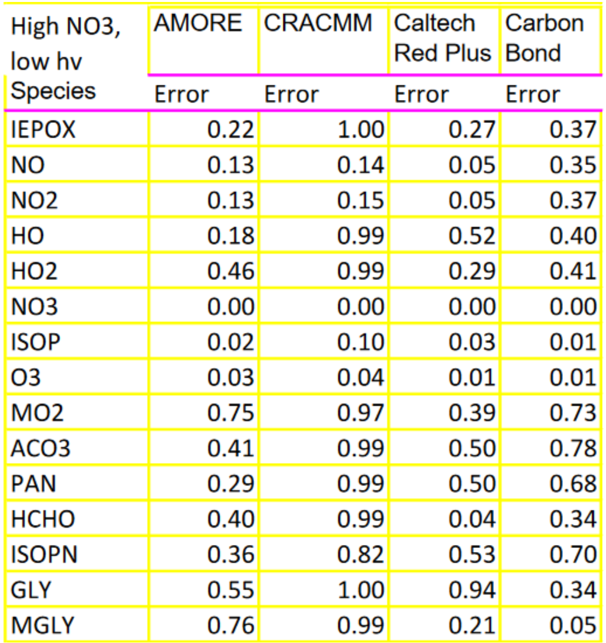


Low NOx	AMORE	CRACMM	Caltech Red Plus	Carbon Bond
Species	Error	Error	Error	Error
IEPOX	0.13	0.42	0.09	0.25
NO	0.25	0.40	0.08	0.32
NO2	0.48	0.62	0.09	0.49
HO	0.28	0.37	0.07	0.32
HO2	0.22	0.54	0.06	0.27
NO3	0.85	0.92	0.18	0.15
ISOP	0.25	0.23	0.05	0.19
O3	0.35	0.35	0.04	0.26
MO2	0.64	0.43	0.15	0.50
ACO3	0.78	0.75	0.22	0.31
PAN	0.89	0.94	0.11	0.57
HCHO	0.28	0.80	0.12	0.23
ISOPN	0.39	0.53	0.11	0.76
GLY	0.72	0.88	0.41	0.43
MGLY	0.71	0.93	0.11	0.34

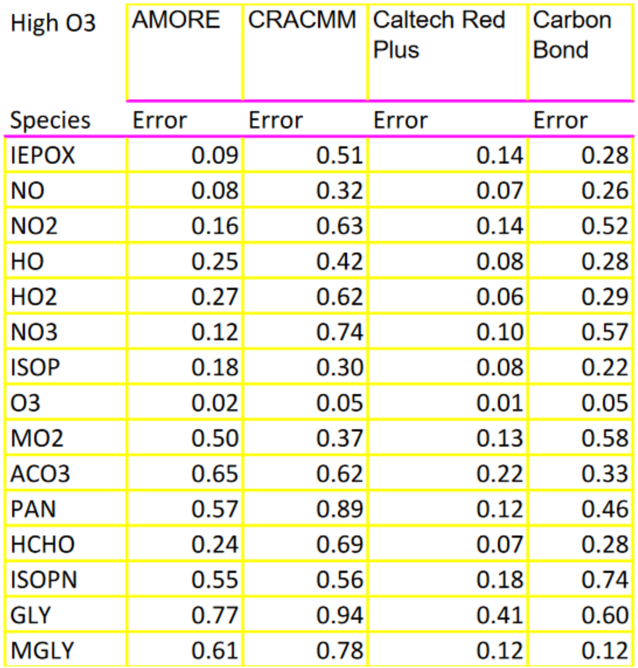
High NOx	AMORE	CRACMM	Caltech Red Plus	Carbon Bond
Species	Error	Error	Error	Error
IEPOX	0.44	0.36	0.02	0.44
NO	0.10	0.11	0.07	0.10
NO2	0.16	0.12	0.08	0.23
HO	0.22	0.09	0.11	0.31
HO2	0.14	0.16	0.03	0.09
NO3	0.37	0.17	0.05	0.36
ISOP	0.12	0.05	0.05	0.12
O3	0.14	0.03	0.03	0.18
MO2	0.28	0.22	0.14	0.40
ACO3	0.41	0.31	0.15	0.16
PAN	0.53	0.41	0.10	0.28
HCHO	0.05	0.50	0.16	0.12
ISOPN	0.27	0.47	0.04	0.92
GLY	0.47	0.53	0.60	0.88
MGLY	0.49	0.31	0.12	0.50



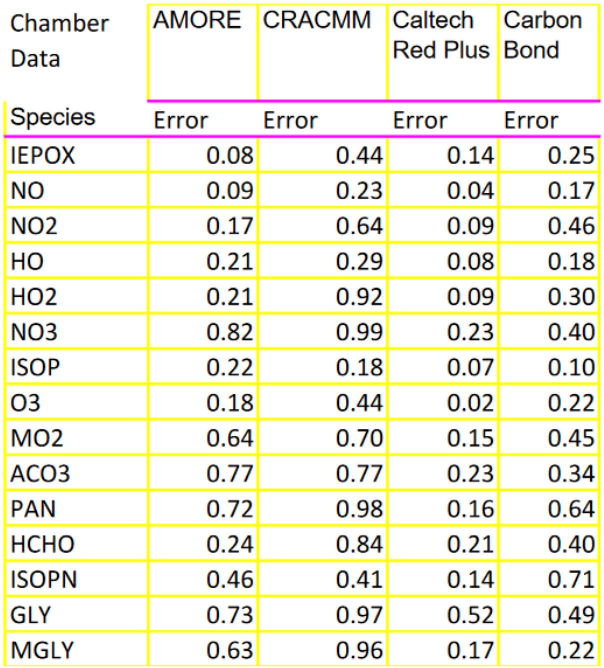
High NO3 Species	AMORE Error	CRACMM Error	Caltech Red Plus Error	Carbon Bond Error
IEPOX	0.08	0.88	0.08	0.06
NO	0.06	0.10	0.02	0.46
NO2	0.06	0.10	0.02	0.46
HO	0.10	0.48	0.15	0.30
HO2	0.42	0.77	0.13	0.36
NO3	0.00	0.00	0.00	0.00
ISOP	0.03	0.20	0.07	0.02
O3	0.01	0.01	0.00	0.01
MO2	0.38	0.83	0.22	0.68
ACO3	0.32	0.86	0.30	0.69
PAN	0.20	0.86	0.28	0.51
HCHO	0.13	0.92	0.08	0.41
ISOPN	0.55	0.89	0.55	0.79
GLY	0.60	0.84	0.71	0.67
MGLY	0.56	0.76	0.08	0.15



High NO3, low hv Species	AMORE Error	CRACMM Error	Caltech Red Plus Error	Carbon Bond Error
IEPOX	0.22	1.00	0.27	0.37
NO	0.13	0.14	0.05	0.35
NO2	0.13	0.15	0.05	0.37
HO	0.18	0.99	0.52	0.40
HO2	0.46	0.99	0.29	0.41
NO3	0.00	0.00	0.00	0.00
ISOP	0.02	0.10	0.03	0.01
O3	0.03	0.04	0.01	0.01
MO2	0.75	0.97	0.39	0.73
ACO3	0.41	0.99	0.50	0.78
PAN	0.29	0.99	0.50	0.68
HCHO	0.40	0.99	0.04	0.34
ISOPN	0.36	0.82	0.53	0.70
GLY	0.55	1.00	0.94	0.34
MGLY	0.76	0.99	0.21	0.05



High O3 Species	AMORE Error	CRACMM Error	Caltech Red Plus Error	Carbon Bond Error
IEPOX	0.09	0.51	0.14	0.28
NO	0.08	0.32	0.07	0.26
NO2	0.16	0.63	0.14	0.52
HO	0.25	0.42	0.08	0.28
HO2	0.27	0.62	0.06	0.29
NO3	0.12	0.74	0.10	0.57
ISOP	0.18	0.30	0.08	0.22
O3	0.02	0.05	0.01	0.05
MO2	0.50	0.37	0.13	0.58
ACO3	0.65	0.62	0.22	0.33
PAN	0.57	0.89	0.12	0.46
HCHO	0.24	0.69	0.07	0.28
ISOPN	0.55	0.56	0.18	0.74
GLY	0.77	0.94	0.41	0.60
MGLY	0.61	0.78	0.12	0.12



Chamber Data Species	AMORE Error	CRACMM Error	Caltech Red Plus Error	Carbon Bond Error
IEPOX	0.08	0.44	0.14	0.25
NO	0.09	0.23	0.04	0.17
NO2	0.17	0.64	0.09	0.46
HO	0.21	0.29	0.08	0.18
HO2	0.21	0.92	0.09	0.30
NO3	0.82	0.99	0.23	0.40
ISOP	0.22	0.18	0.07	0.10
O3	0.18	0.44	0.02	0.22
MO2	0.64	0.70	0.15	0.45
ACO3	0.77	0.77	0.23	0.34
PAN	0.72	0.98	0.16	0.64
HCHO	0.24	0.84	0.21	0.40
ISOPN	0.46	0.41	0.14	0.71
GLY	0.73	0.97	0.52	0.49
MGLY	0.63	0.96	0.17	0.22

Comment 27:

Section 3.2 (box model comparisons) is very short considering this is the first comparison of the mechanism to real data. The authors state that the "Caltech Full mechanism matched the concentrations of all measured species from the chamber study" but provide no evidence of this. It would be good to see some plots of major species of interest with the modelled and measured data included. This is especially necessary since their "Caltech full mechanism" is an adaptation of the published Caltech mechanism, so has the potential to show important differences. Including this data would also allow for a comparison of the new mechanism to measured data for species other than IEPOX (e.g. how does it do for the species groups listed in Table 5?). This is a very limited comparison to one specific chamber experiment under specific conditions. Why have the authors not compared to other isoprene chamber data? There must be significant amounts of isoprene chamber experiments available in the ICARUS (**https://icarus.ucdavis.edu**) and ACTRIS/EUROCHAMP (**https://data.eurochamp.org**) chamber databases.

As mentioned in the response to Comment 6, the Wennberg et al. 2018 Caltech Full isoprene mechanism and its reduced versions are widely used and have been validated previously. We have made further efforts to validate the extended Full mechanism in comparison to the Wennberg et al. 2018 mechanism and chamber data, as described above in the response to Comment 6 and section S.1.

Comment 28:

Similarly, in **Section 3.3**, the authors only show comparisons for formaldehyde and O3. Although they state that there were no changes for NOy, OC, and HNO3, it would be good to see plots of this (probably in the SI).

These plots have been added to the section S.16. This section has been added here for reference:

"Additional CMAQ results are shown in figure S.12. These plots show the binned bias of the AMORE mechanism for different ranges of the measured value. All measurements are part of the LISTOS campaign. The AMORE mechanism (red) is shown in comparison to the CRACMM1 base mechanism (gray) and a prior version of the AMORE mechanism (blue).

The AMORE mechanism shows slightly very slightly increased OC concentrations and slightly decreased isoprene concentrations, however the difference is not significant. There is no discernible difference in the NOy concentrations between the three mechanisms. Due to issues with the CMAQ run boundary conditions, the overall magnitude of the bias is confounded by many factors unrelated to isoprene. Thus, the main conclusion to be drawn from these graphs is that there is no significant change from the base mechanism.

Figure S.12.a) CMAQ isoprene biases

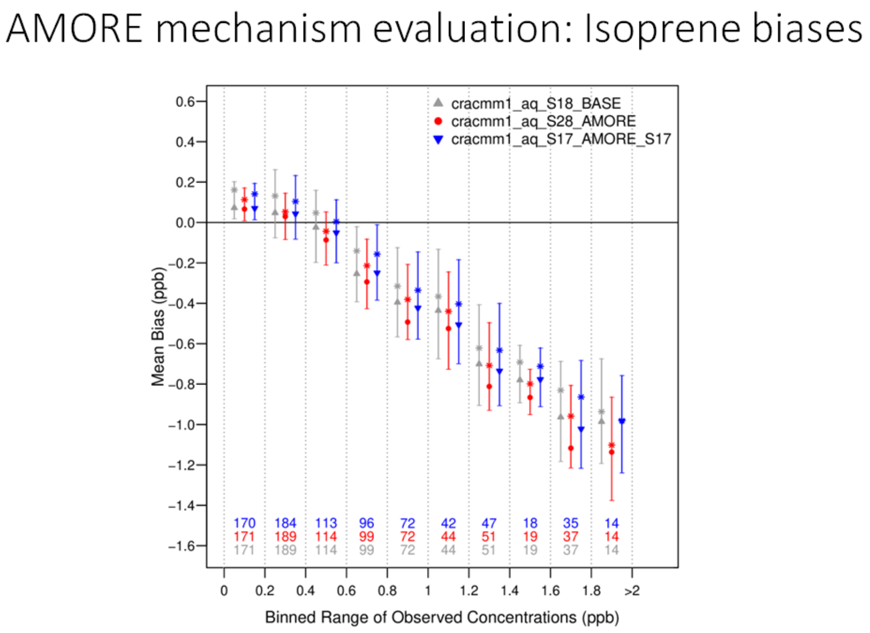


Figure S.12.b) CMAQ NOy biases

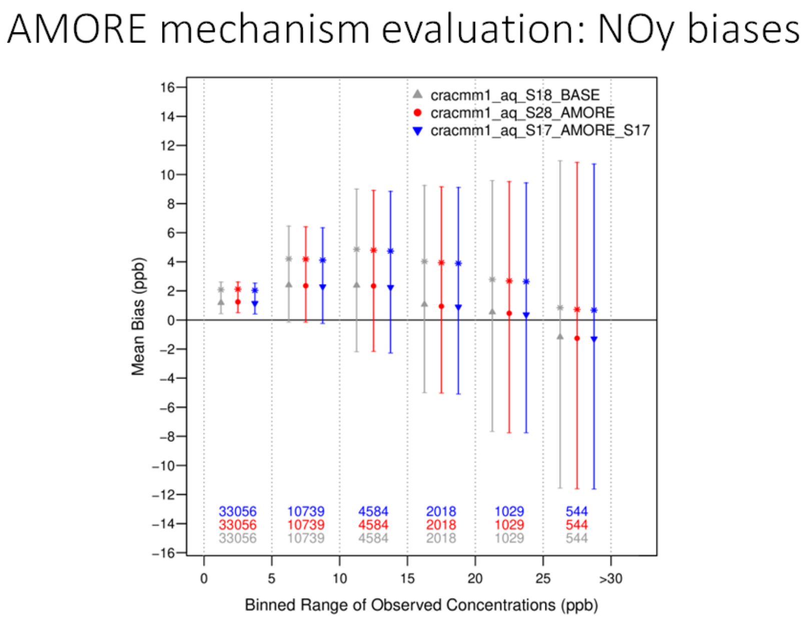
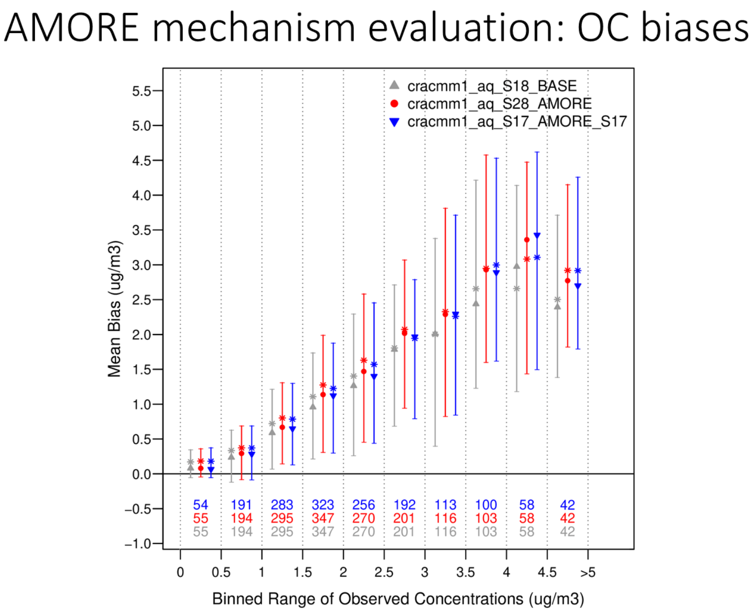


Figure S.12.c) CMAQ OC biases



Comment 29:

One final comment… The authors demonstrate the use of graph theory for the (significant) reduction of complex chemical mechanisms.What would be the outcome if you started from using the reduced form of the CalTech mechanism?

We have not run the algorithm or made a mechanism from the Caltech reduced mechanism, though it should produce nearly identical results given the agreement between the Caltech reduced and full mechanisms. Due to the design of the algorithm, the size of the reduced mechanism would have been the same with either input mechanism, so the more accurate full mechanism was used.

Reviewer 2

Comment 1:

The authors present a work describing the construction of a very reduced isoprene oxidation mechanism by use of an original semi-automatic algorithm also developed by the authors. The manuscript is well written, and the reduction algorithm is explained well. I only have concerns (detailed below) model performance at low NO conditions.

We are grateful to the reviewer for this positive assessment of our work and the manuscript.

Comment 2:

The mechanism presented has not been developed and tested for real low NO conditions (< 200 ppt) that are not that seldom in high-isoprene environments.

Based on the comments of both reviewers, we have investigated an expanded range of conditions (including elevated values for NO, NO_2, and OH) both for assessing the performance of AMORE Isoprene 1.0 and for assessing the sensitivity of the AMORE algorithm. Performance of AMORE Isoprene 1.0 is similar to the Caltech full mechanism for NO_x, OH, and ozone at very low NO_x concentrations, giving us confidence that this mechanism is suitable for low and high NO_x scenarios.

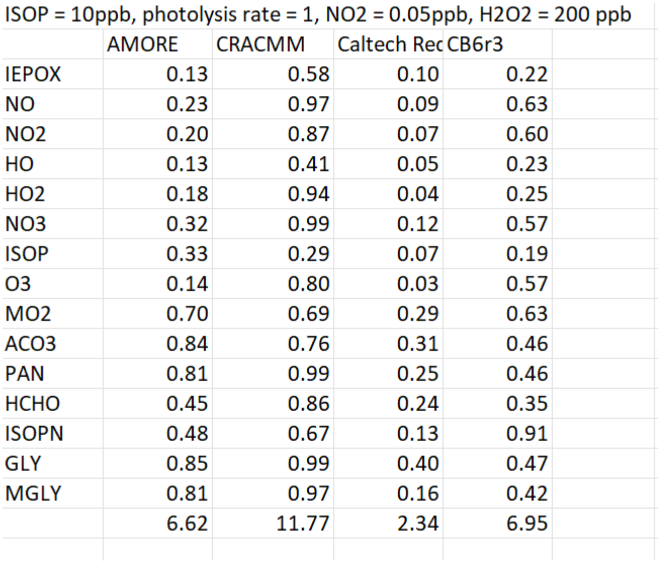
An additional test was run with NO_x = 0.05 ppb (t = 0). Under these conditions, the overall mechanism performance was similar to other conditions. Error tables for low NO_x are shown in supplement section 15, Table S.7 and Figure S.9. Here is section S.15 for reference:

"S.15. Additional AMORE Box Model Simulations

Only six testing conditions were shown in the box model testing for the AMORE-Isoprene mechanism. Here we include additional box model results at more extreme conditions that are not well represented in the six main testing conditions. From these additional tests, we conclude that the AMORE-Isoprene mechanism is suitable for these additional extreme conditions.

The first additional testing condition was with very low NO_x concentrations. The initial NO_2 concentration was set to 0.05 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2 and ozone are provided as well. At low NO_x, the AMORE-Isoprene mechanism continues to have low error for OH, NO_x, O_3, and other important species. As demonstrated by Figure S.9 and Table S.7, the AMORE is the most accurate small mechanism in these conditions.

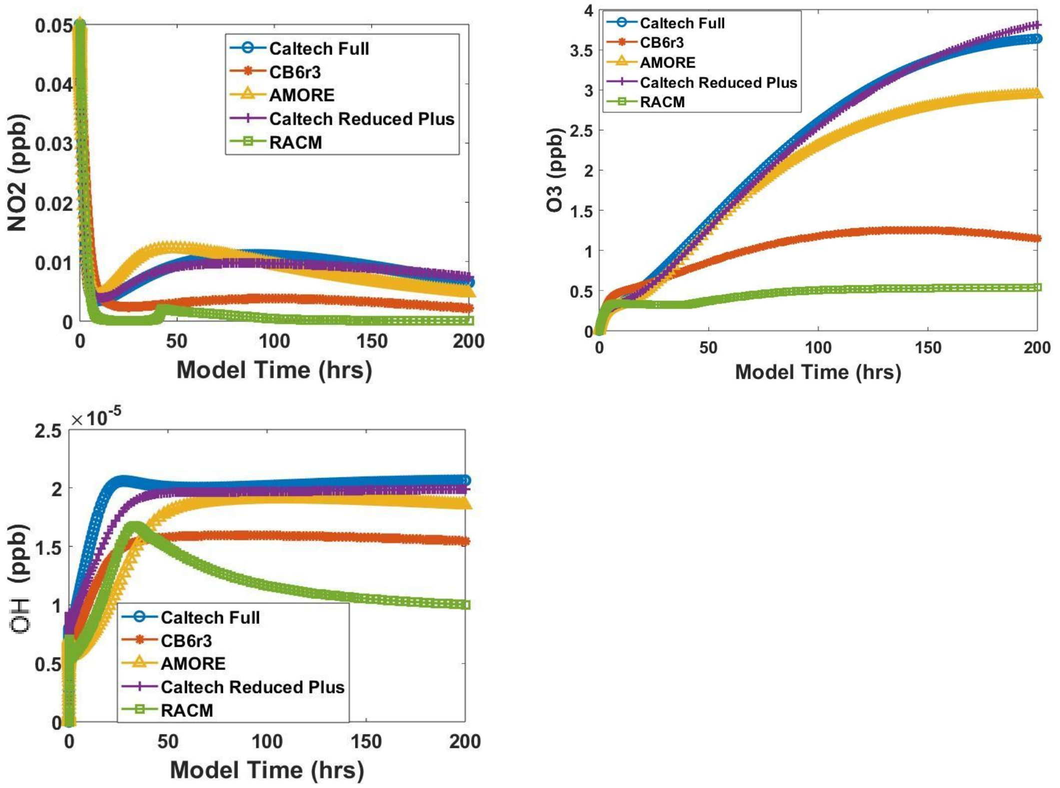
Table S.7 Very low NO_x error table



ISOP = 10ppb, photolysis rate = 1, NO2 = 0.05ppb, H2O2 = 200 ppb

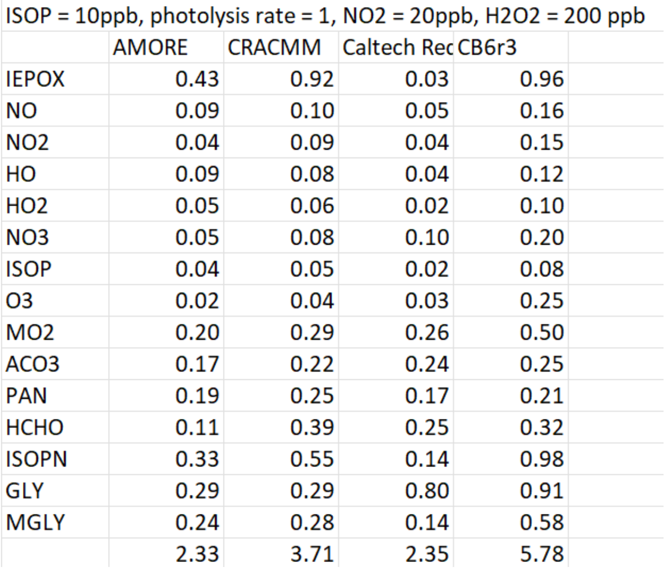
	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.13	0.58	0.10	0.22
NO	0.23	0.97	0.09	0.63
NO2	0.20	0.87	0.07	0.60
HO	0.13	0.41	0.05	0.23
HO2	0.18	0.94	0.04	0.25
NO3	0.32	0.99	0.12	0.57
ISOP	0.33	0.29	0.07	0.19
O3	0.14	0.80	0.03	0.57
MO2	0.70	0.69	0.29	0.63
ACO3	0.84	0.76	0.31	0.46
PAN	0.81	0.99	0.25	0.46
HCHO	0.45	0.86	0.24	0.35
ISOPN	0.48	0.67	0.13	0.91
GLY	0.85	0.99	0.40	0.47
MGLY	0.81	0.97	0.16	0.42
	6.62	11.77	2.34	6.95

Figure S.9 Very low NO_x (0.05 ppb) simulation, NO_2 and O_3 Plots



The second additional testing condition was with very high NO_x concentrations. The initial NO_2 concentration was set to 20 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2 and ozone are provided as well. The results show that AMORE has strong agreement with the Caltech full mechanism for both ozone, NO_2, and many other *species (see error table). This suggests that the AMORE isoprene mechanism is suitable for high NO_x conditions.*

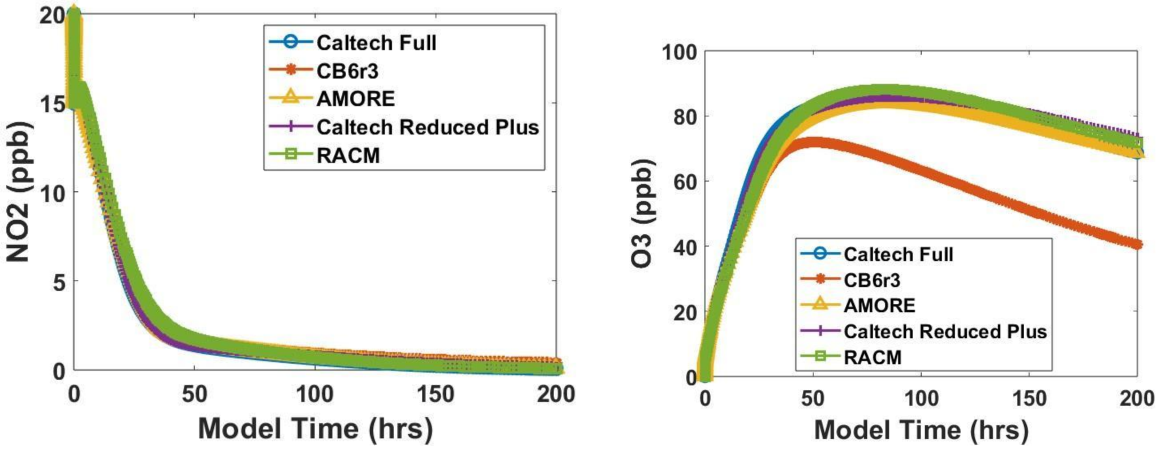
Table S.8. Very high NO_x error table



ISOP = 10ppb, photolysis rate = 1, NO2 = 20ppb, H2O2 = 200 ppb

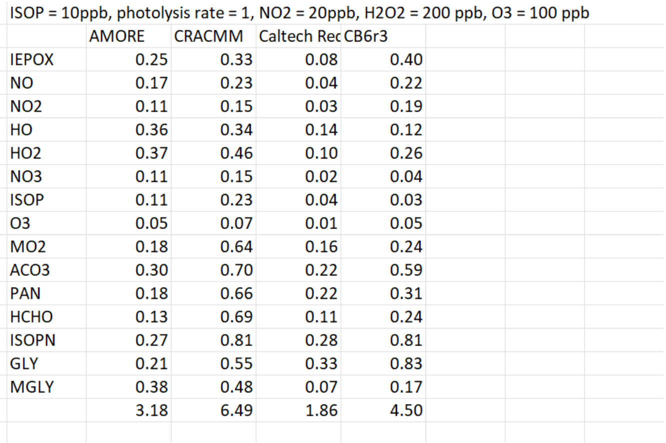
	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.43	0.92	0.03	0.96
NO	0.09	0.10	0.05	0.16
NO2	0.04	0.09	0.04	0.15
HO	0.09	0.08	0.04	0.12
HO2	0.05	0.06	0.02	0.10
NO3	0.05	0.08	0.10	0.20
ISOP	0.04	0.05	0.02	0.08
O3	0.02	0.04	0.03	0.25
MO2	0.20	0.29	0.26	0.50
ACO3	0.17	0.22	0.24	0.25
PAN	0.19	0.25	0.17	0.21
HCHO	0.11	0.39	0.25	0.32
ISOPN	0.33	0.55	0.14	0.98
GLY	0.29	0.29	0.80	0.91
MGLY	0.24	0.28	0.14	0.58
	2.33	3.71	2.35	5.78

Figure S.10 Very high NO_x (20 ppb) simulation, NO_2 and O_3 Plots



The final additional testing condition was with very high NO_x concentrations and high ozone concentrations. The initial NO_2 concentration was set to 20 ppb and the initial ozone concentration was set to 100 ppb. The rest of the testing inputs are shown in the error table provided below. Plots of NO_2, OH, and ozone are provided as well. At high ozone and NO_x, the AMORE mechanism shows strong agreement for both ozone, NO_2, and OH concentrations (Figure S.10), and low error for most species (Table S.9). This suggests that the AMORE mechanism is suitable for high NO_x and high Ozone conditions.

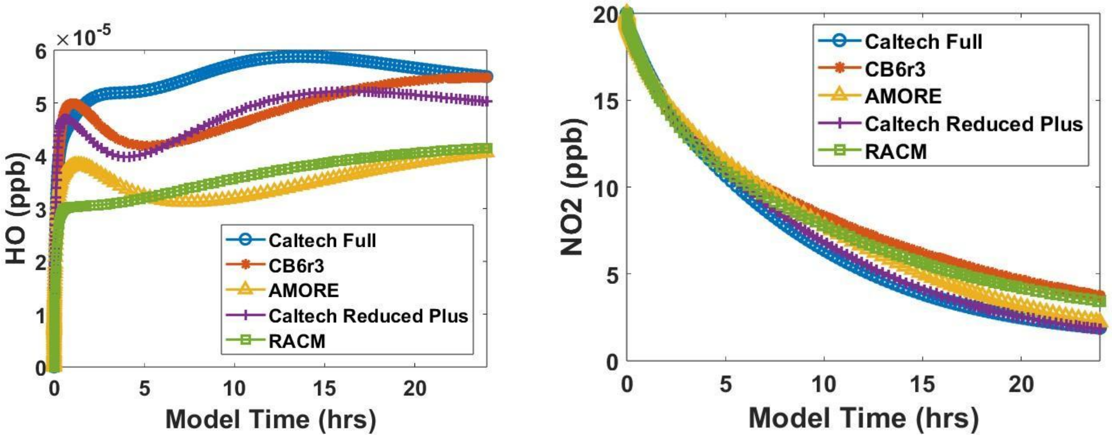
Table S.9 Very high NO_x and high ozone error table

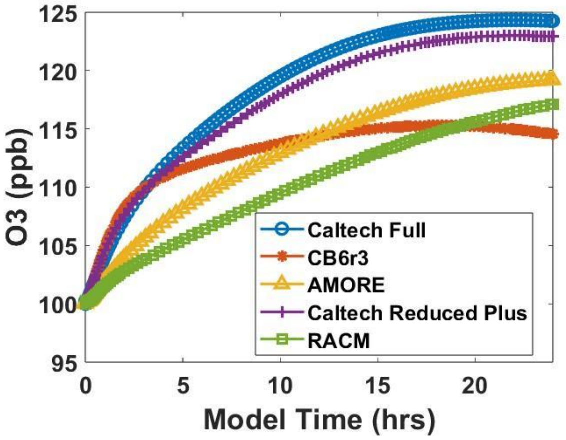


ISOP = 10ppb, photolysis rate = 1, NO2 = 20ppb, H2O2 = 200 ppb, O3 = 100 ppb

	AMORE	CRACMM	Caltech Rec	CB6r3
IEPOX	0.25	0.33	0.08	0.40
NO	0.17	0.23	0.04	0.22
NO2	0.11	0.15	0.03	0.19
HO	0.36	0.34	0.14	0.12
HO2	0.37	0.46	0.10	0.26
NO3	0.11	0.15	0.02	0.04
ISOP	0.11	0.23	0.04	0.03
O3	0.05	0.07	0.01	0.05
MO2	0.18	0.64	0.16	0.24
ACO3	0.30	0.70	0.22	0.59
PAN	0.18	0.66	0.22	0.31
HCHO	0.13	0.69	0.11	0.24
ISOPN	0.27	0.81	0.28	0.81
GLY	0.21	0.55	0.33	0.83
MGLY	0.38	0.48	0.07	0.17
	3.18	6.49	1.86	4.50

Figure S.11 Very high NO_x (20 ppb) and high ozone (100 ppb) simulation, NO_2, OH, and O_3 Plots





In general, unimolecular decompositions are not considered among the “oxidation pathways”.

This is correct. The algorithm did not include the option for unimolecular decompositions.

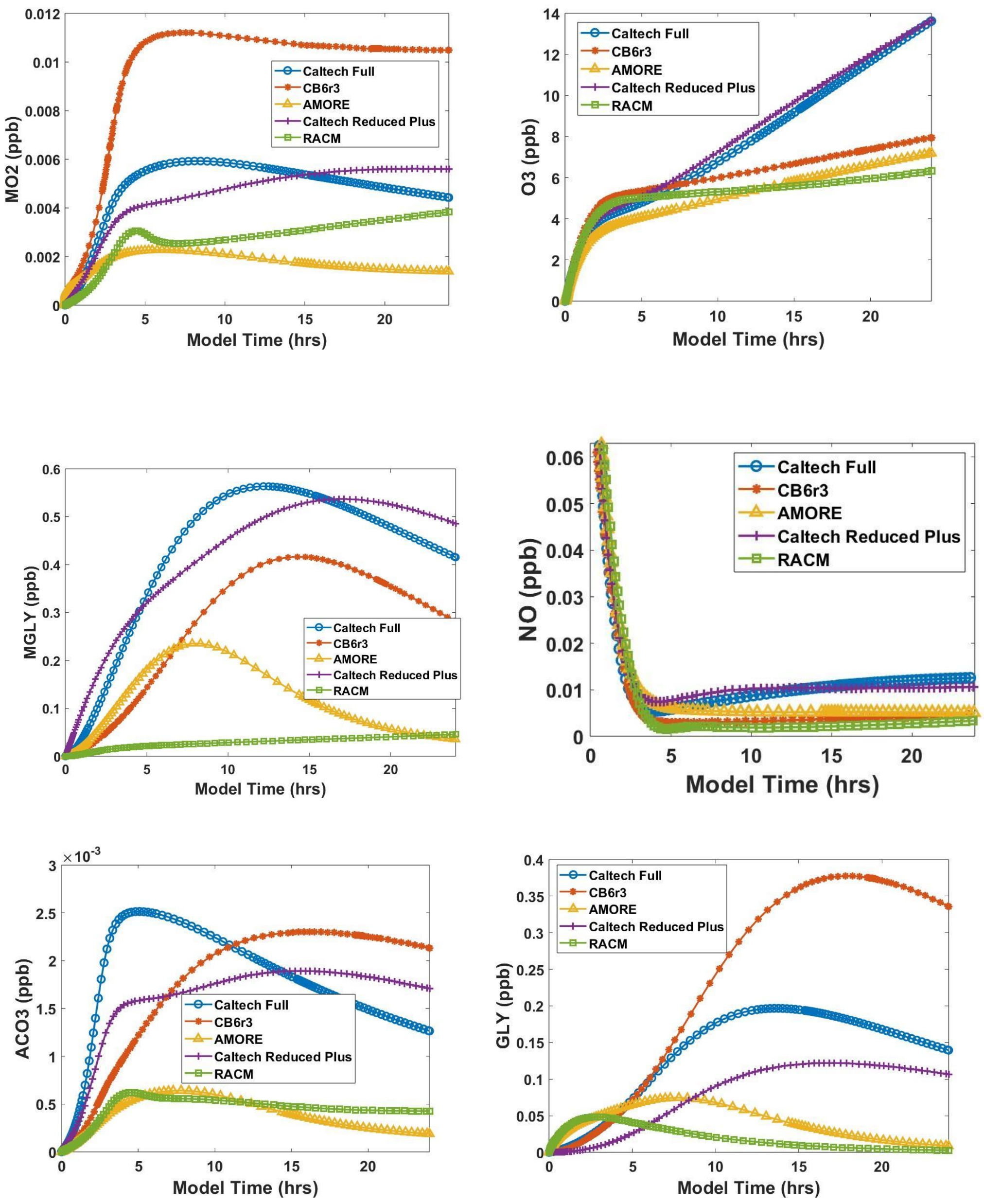
However, Bates and Jacob (2019) report ISOPO2 isomerization to be 22% of the total loss on average. Reaction 2 in Table S.2 look like to be such a unimolecular reaction, but it is not found in the final mechanism. This is likely to be the main reason the authors need to add 0.6 HO2 to the ISOP + HO2 reaction in order to improve the comparisons with the Caltech mechanism as shown in Fig. 3. However, the comparison for ambient conditions is presented for HO2 and HCHO only. The deviations of AMORE are not small but may be accepted given the extreme computational cost saving. What is worrying is the absence of a comparison for predicted OH, especially at low NO. It is by now well known that photolysis of HPALDs and other H-shifts (unimolecular decompositions) are key in determining OH-recycling and OH levels under relevant atmospheric conditions. The authors should show a comparison for OH.

See response below for the OH figure. We have included a new figure showing the same tests for OH, including our low NO condition. As you highlighted earlier, conditions with NO_x < 200 ppt are not represented in our original set of conditions. While we have not added a lower NO_x condition to our tables in the main paper, we ran additional tests with low NO_x (50 ppt) and added the results to the supplement (section S.15). The graph of OH concentrations under very low NO_x conditions is shown in Figure S.9.

I mean, model bias reduction for ozone and formaldehyde simulated by CMAQ are significant (as shown in Sect. 3.3) but I wonder that could be partly for the wrong reasons. For instance, at low O3 the model bias worsens. Why is that? Anyway, errors in predicting OH cause errors in magnitude and timing of VOC oxidation and SOA production. A hint could be provided if plots like the ones in Fig. 3 and 4 were done for OH and ISOP.

Figure 4 has been replicated for isoprene, along with ozone, NO, NO_2, MGLY and GLY. Here are those plots:

Figure S.15. Low NO_x



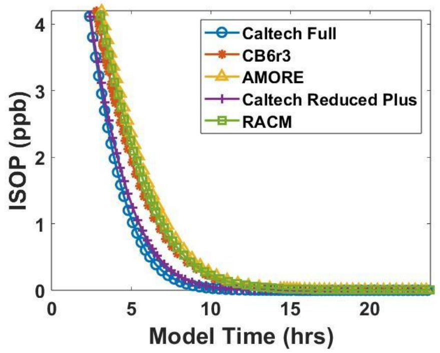
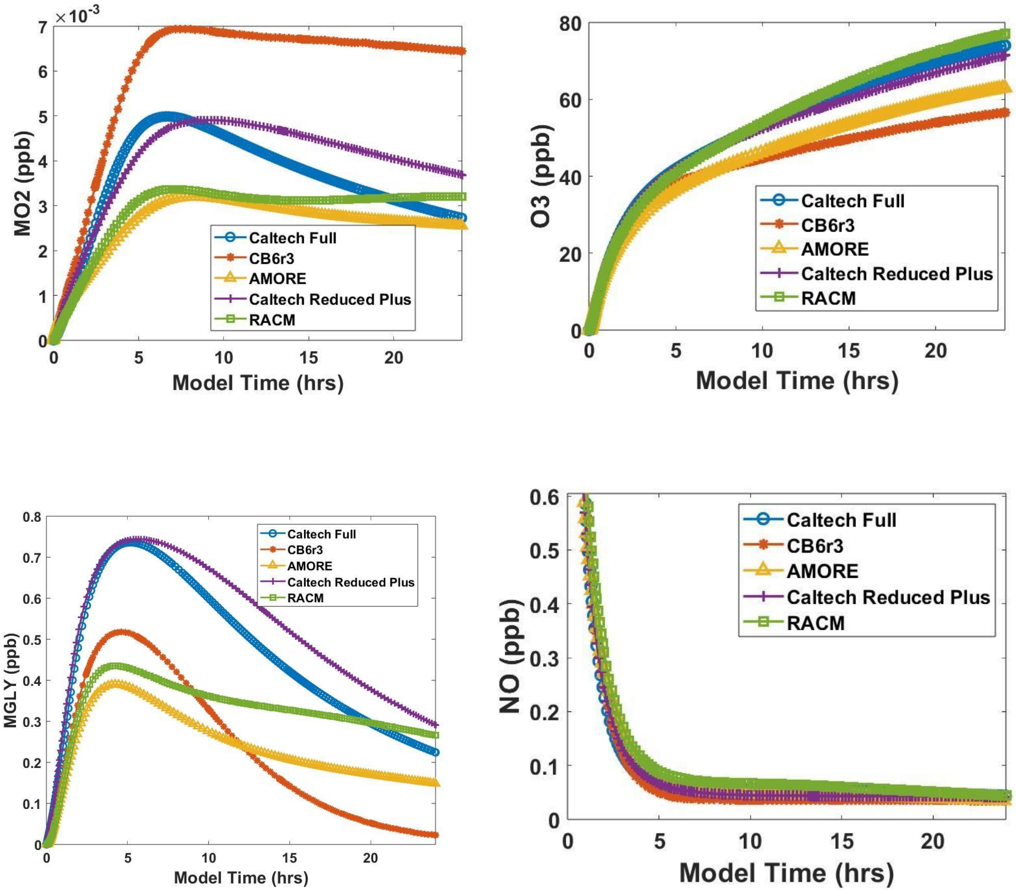


Figure S.16. High NO_x



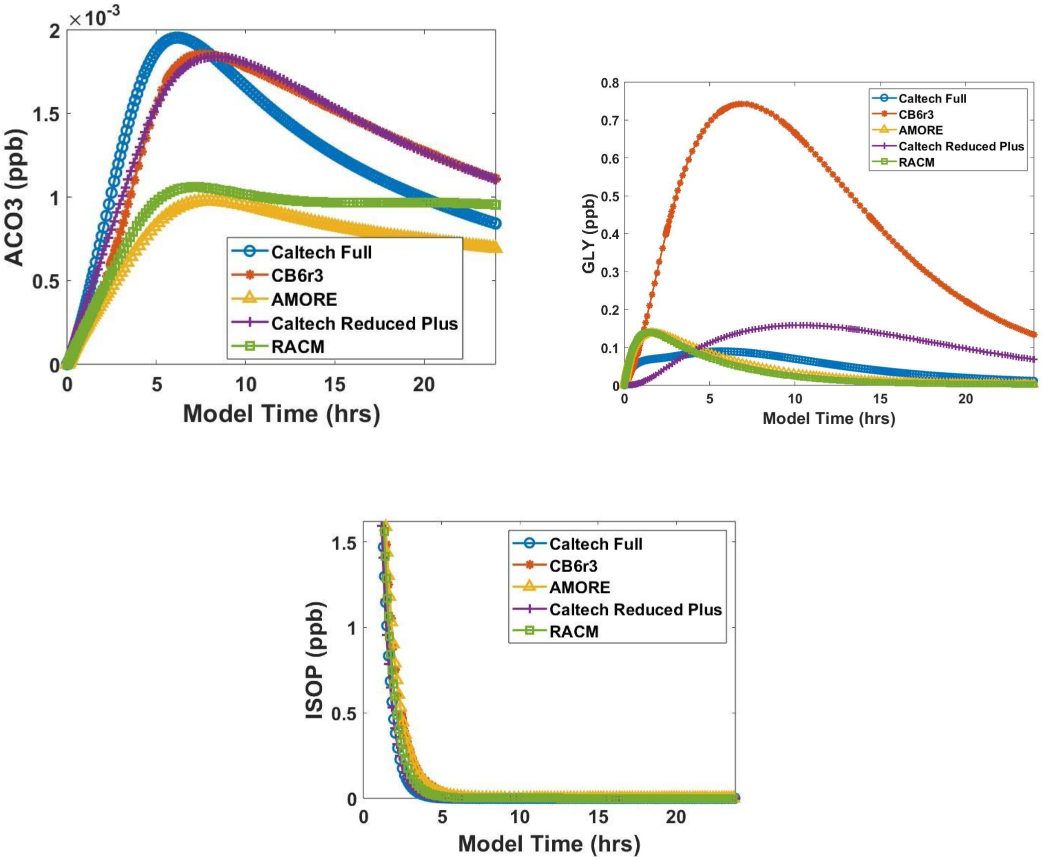
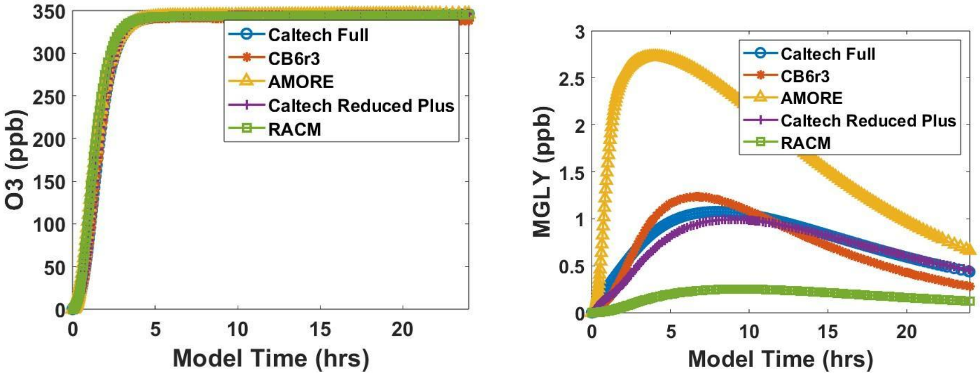
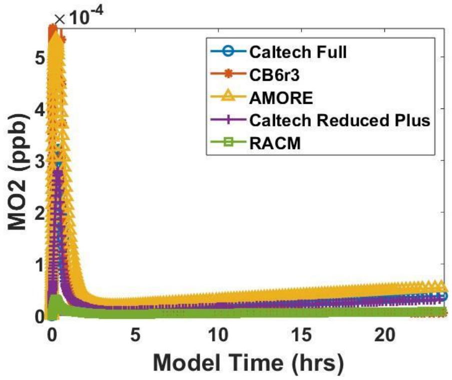
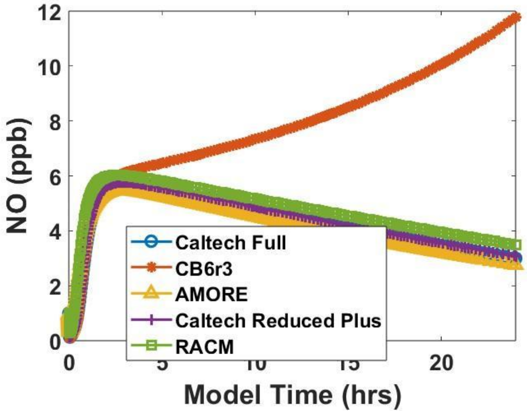
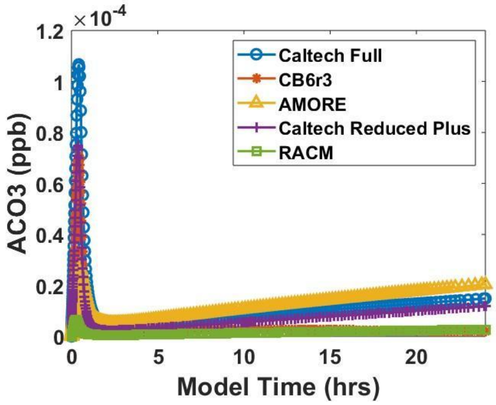


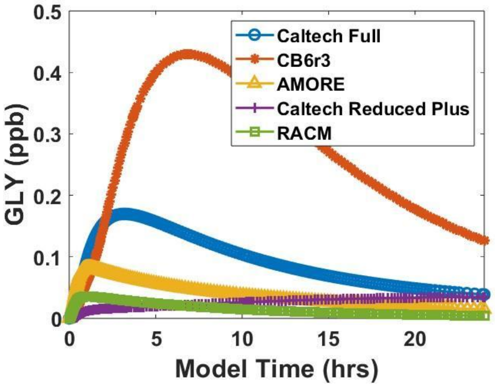
Figure S.17. High NO_3




×10^-4
MO2 (ppb)
0
1
2
3
4
5
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


NO (ppb)
0
2
4
6
8
10
12
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


×10^-4
ACO3 (ppb)
0
0.2
0.4
0.6
0.8
1
1.2
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


GLY (ppb)
0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

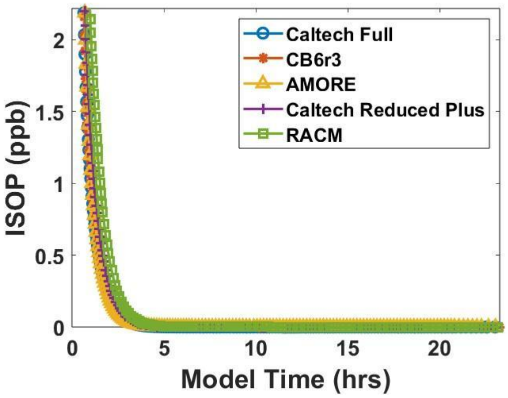
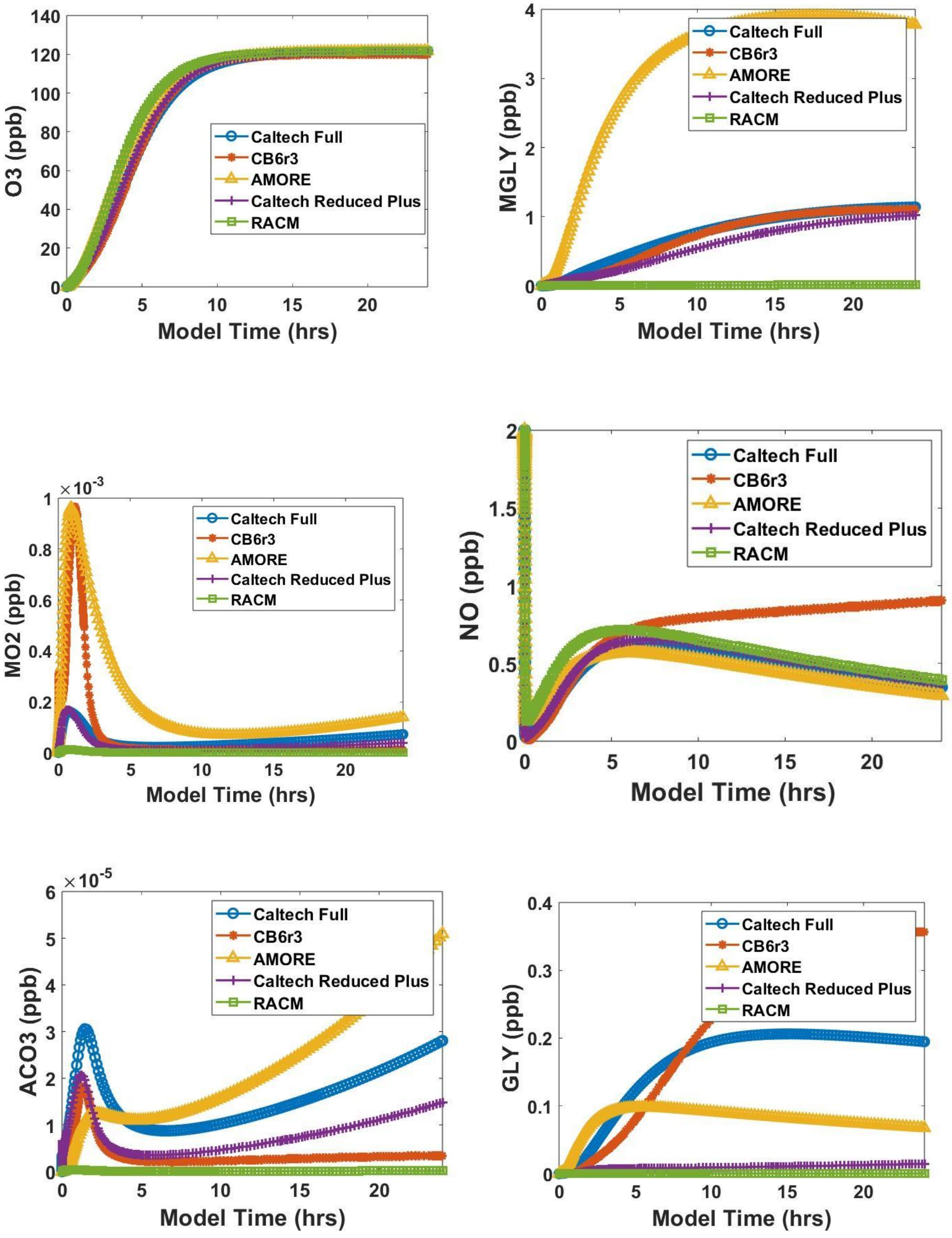

ISOP (ppb)
0
0.5
1
1.5
2
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

Figure S.18. High NO$_3$ low hv



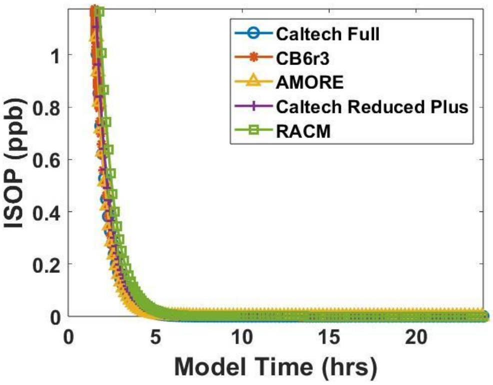
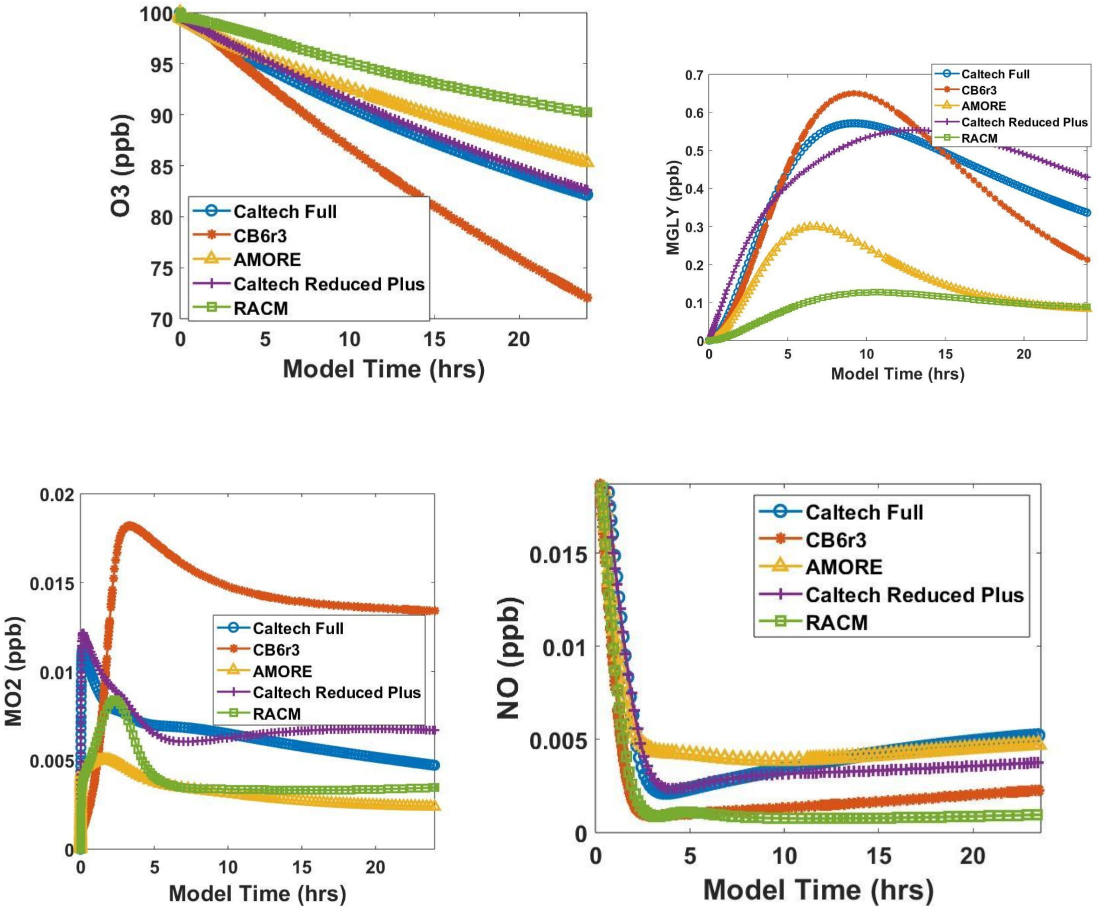


Figure S.19. High O_3



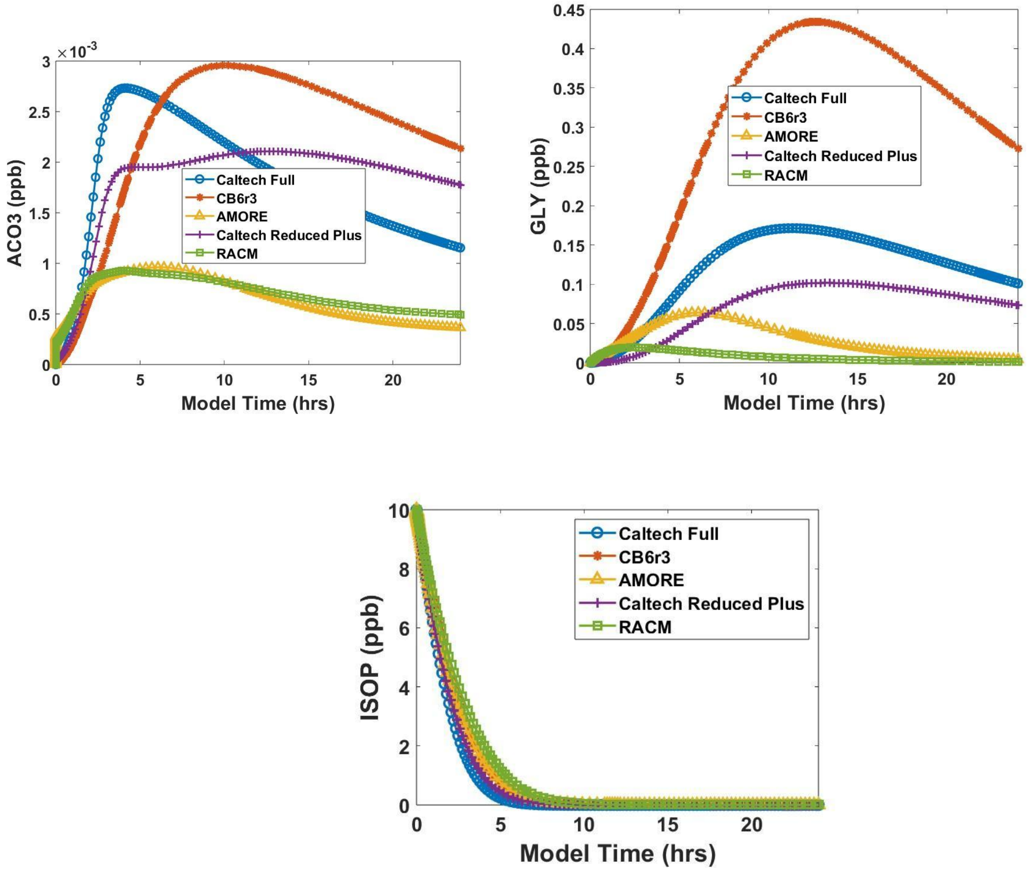
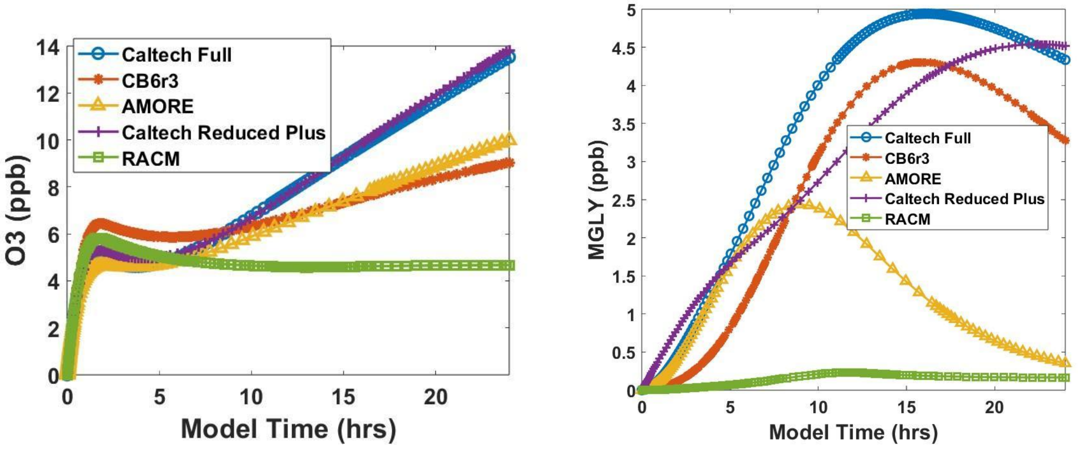
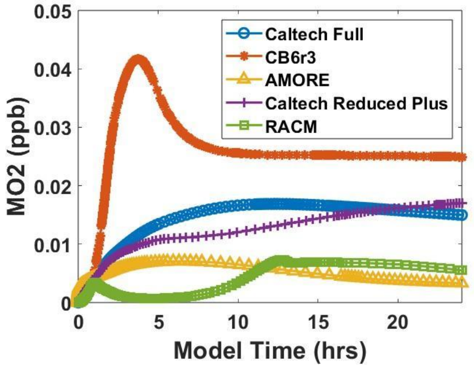
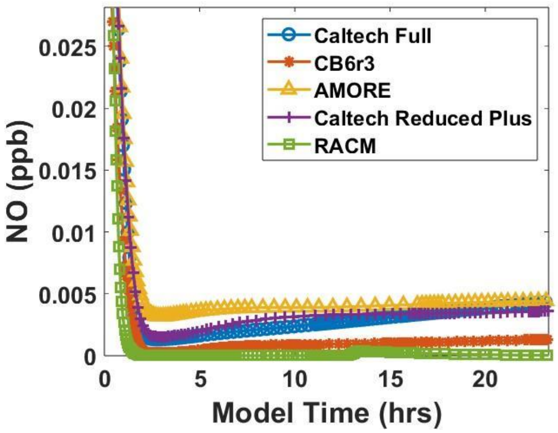
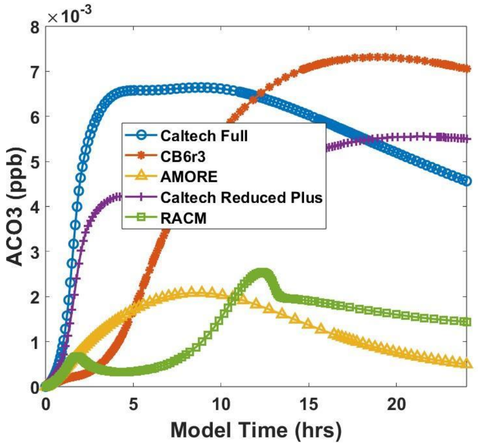


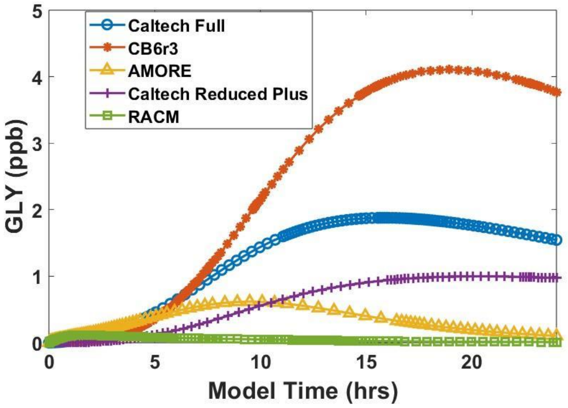
Figure S.20. Chamber Comparison




MO2 (ppb)
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


NO (ppb)
0.025
0.02
0.015
0.01
0.005
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


×10-3
ACO3 (ppb)
8
7
6
5
4
3
2
1
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM


GLY (ppb)
5
4
3
2
1
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

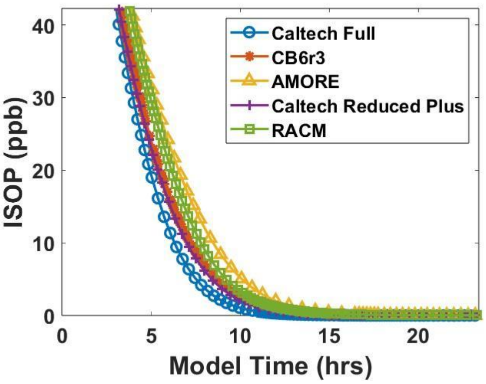
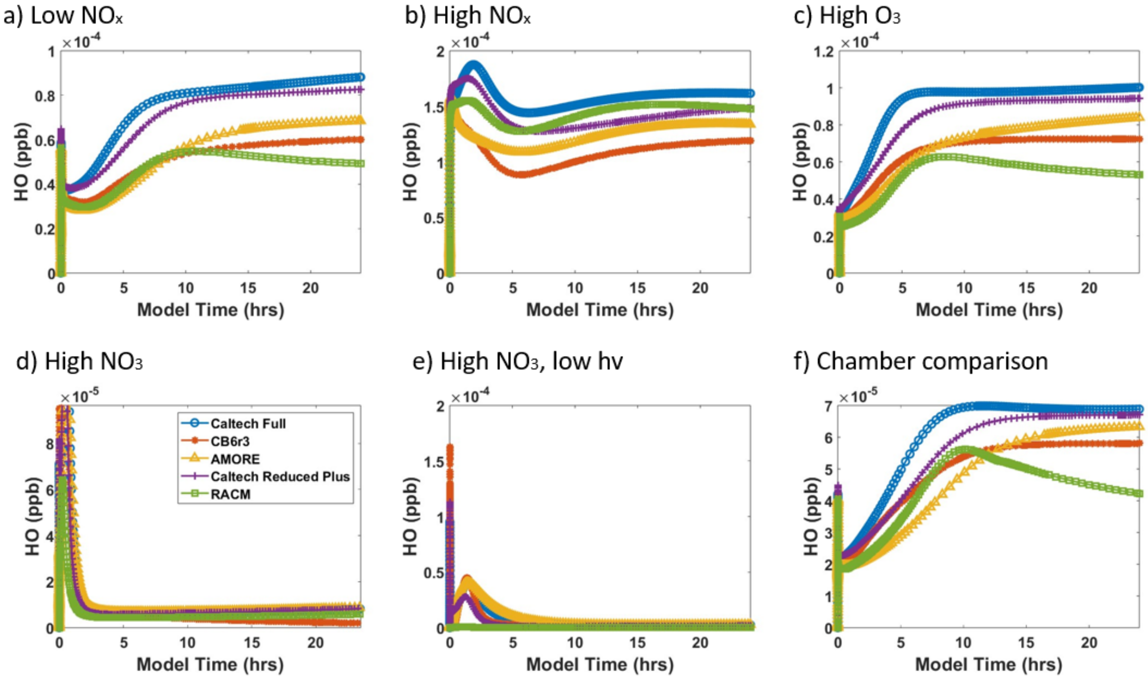

ISOP (ppb)
40
30
20
10
0
0
5
10
15
20
Model Time (hrs)
Caltech Full
CB6r3
AMORE
Caltech Reduced Plus
RACM

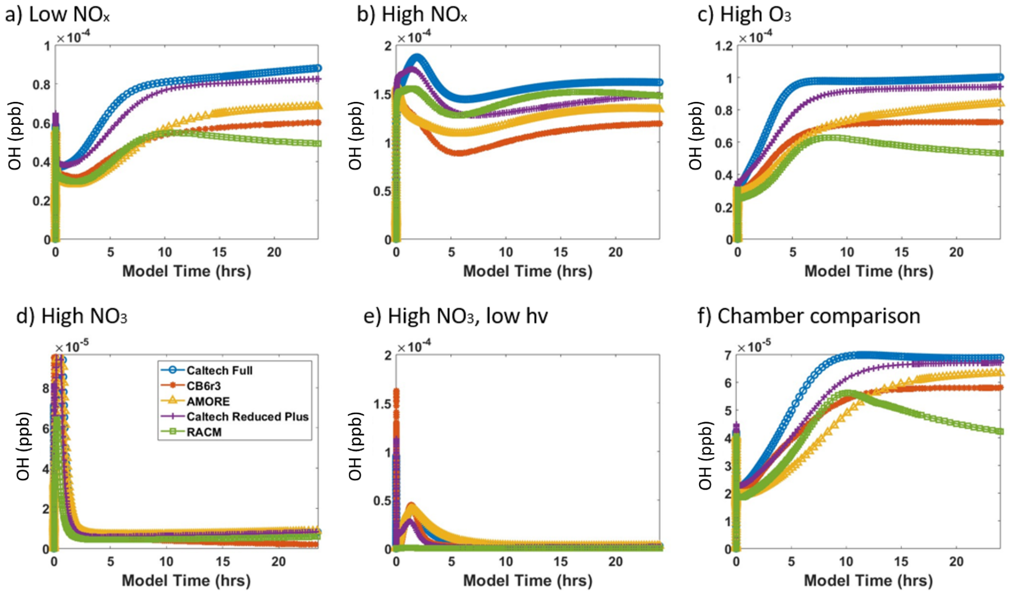
Figure 6, a new figure based on figure 4 has been created for OH in the main paper, and the following discussion of the plot has been added:



"Figure 6 shows the simulated concentration of the hydroxyl radical under the six conditions listed in Table 3. The AMORE- isoprene mechanism performs similarly to other highly reduced mechanisms. As with other small mechanisms, AMORE-Isoprene is biased low compared to the full Caltech mechanism. Under low NO_x conditions, the AMORE-Isoprene mechanism has similar behavior to CB6r3 and RACM2 at short time frames and has a more accurate steady state value at longer times. At high NO_x, the RACM2 mechanism is the most accurate small mechanism, with AMORE-Isoprene having close but slightly lower OH concentrations. At high O3, AMORE-Isoprene has the closest agreement with the Caltech full mechanism. The Caltech Reduced plus mechanism has strong agreement with the full mechanism at all tested conditions, as would be expected. The main reason for the discrepancy in between AMORE-Isoprene and the Caltech full mechanism in hydroxyl radical concentrations is that the Caltech full mechanism has a greater quantity of intermediate species which produce and consume OH. On balance, this leads to slightly higher hydroxyl radical concentrations, and given that the AMORE-Isoprene mechanism is a much smaller mechanism, there are limitations to the extent that this can be corrected. This is further evidenced by the fact that the other small mechanisms have similar low biased hydroxyl radical concentrations. Overall, the AMORE-Isoprene mechanism performs consistently well at

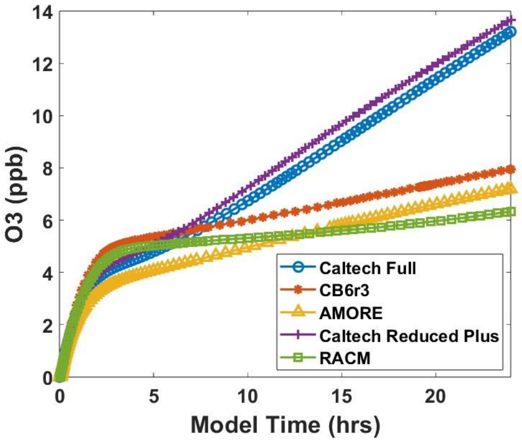
predicting OH concentrations, and is in line with similarly sized mechanisms in this regard."

The CRACMM1 base isoprene mechanism (RACM2) and AMORE-Isoprene have generally similar OH concentrations. Both are biased low compared to the Caltech full mechanism. At lower NO_x, the AMORE-Isoprene has slightly better agreement with the Caltech full mechanism, and at high NO_x, the RACM2 mechanism has slightly better agreement with the Caltech full mechanism. Both mechanisms do a reasonable job of following the Caltech full mechanism and shouldn't lead to any significant change in the timing of VOC or SOA production.

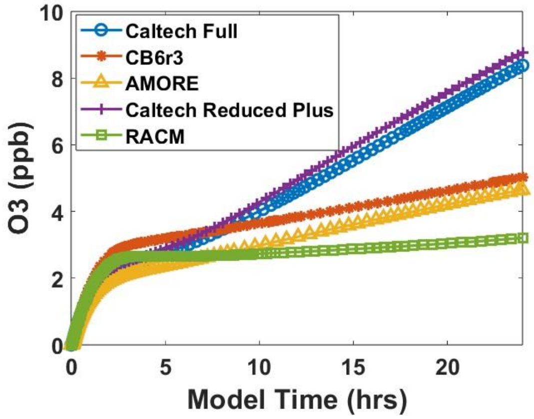


In our CMAQ simulation, O3 model bias worsened at low O3 concentrations. O3 concentrations were already biased high in base CMAQ-CRACMM at low O3 concentrations prior to our updates. The plots below of O3 at different NO concentrations illustrate that AMORE has higher O3 values than the RACM2 mechanism used as the baseline in the CMAQ-CRACMM simulations. Thus, the base overestimates of O3 are worsened in AMORE. However, the AMORE mechanism is in stronger agreement with the Caltech full mechanism giving us confidence that it is a better representation of isoprene chemistry. Lower ozone concentrations are expected at night and thus will be sensitive to the representation of the nocturnal planetary boundary layer height and mixing. Low ozone may also occur at the boundaries of the domain and thus set by boundary condition values rather than chemistry. We refer the reader to a future publication (Place et al. 2023, *in prep*) that includes ozone predictions from two additional chemical mechanisms and provides further insight into ozone biases across spatial and temporal scales.

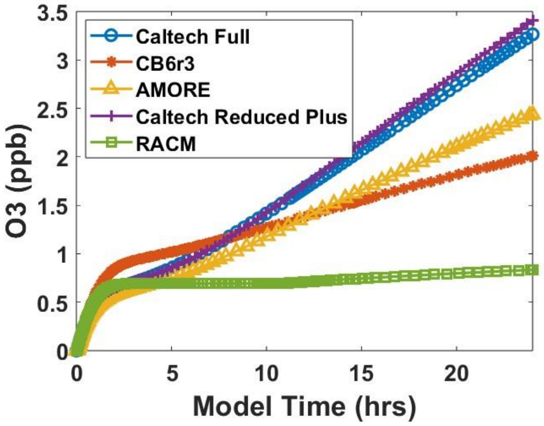
NO = 0.5 ppb



NO = 0.3 ppb

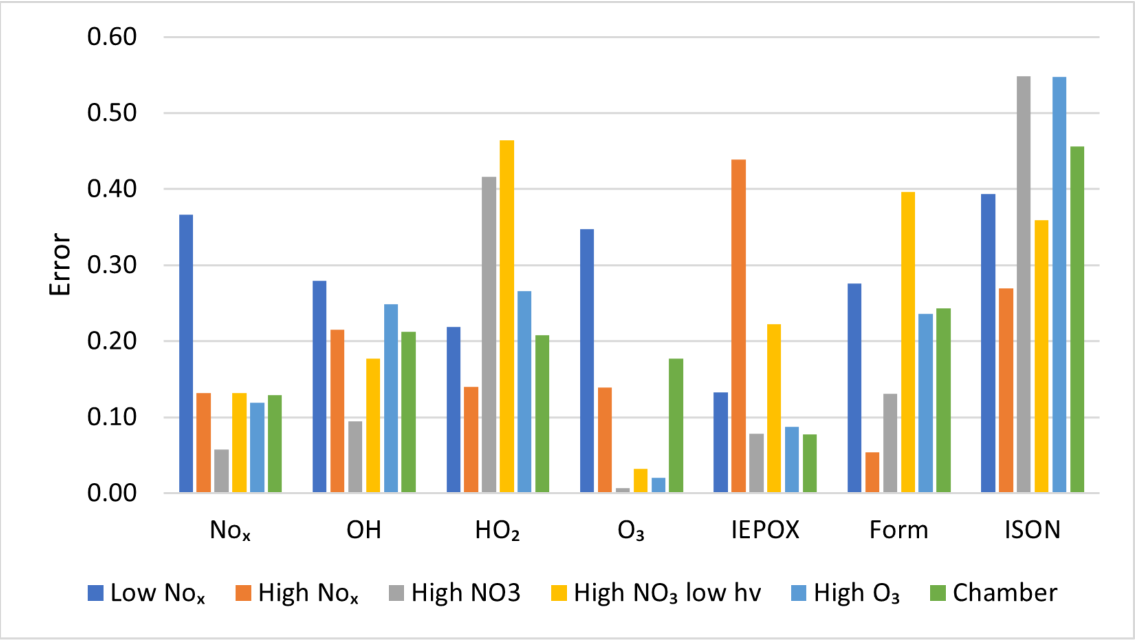


NO = 0.1 ppb



In Fig. 6 the error for "HOx" should be split in the error for OH and HO2.

The change has been made. Due to the additional column, the formatting of the chart has been changed slightly as well. Here is the updated figure:



Comment 3:

The pathway importance algorithm is said to be very sensitive to initial conditions (p. 9, l.219). However, the elevated values for mixing ratios of OH and NO2 does not seem to be give a balanced breadth of atmospheric conditions. Measurements of OH and NO2 often exceed the respected elevated values in Table 2 (2.5E6 molec/cm3 and 10 ppt, respectively). I would like to see how the results change by using values like 1E7 molec/cm3 and 1ppb for OH and NO2, respectively.

We ran the pathway importance algorithm with these suggested inputs. The details of those results are given in the new supplementary section S.13. Here is this section for reference:

“13. Effects of Changing inputs on Pathway Importance Algorithm

The mechanism developed in Table S.5. The header column describes the changes made to the elevated value inputs to the algorithm. There were seven paths that remained unchanged for all inputs. These include {sol}, {O_3}, {NO_3}, {NO_3, sol}, {OH}, {NO}, and {OH, NO}. All other paths listed were only present in some versions of the inputs. For example, the path {NO, NO_2, NO_3} was only present when NO_2 concentrations were elevated to 5 ppb. When OH concentrations were elevated to 10^{-3} ppb (1 ppt, ~2.46 x 10^7 mol/cm^3), the overall number of OH paths decreased. This is likely because OH overshadowed other complementary species, causing their importance to be reduced while the {OH} path increased. All other changes are shown in the table.

Table S.5 Green indicates included path, red indicates unincluded path.

Pathway	Default values	NO = 5 ppb, NO_2 = 2 ppb	NO = 5 ppb, NO_2 = 5 ppb	OH = 10^{-3} ppb
{sol}	🟩	🟩	🟩	🟩
{O_3}	🟩	🟩	🟩	🟩
{NO_3}	🟩	🟩	🟩	🟩
{NO_3, sol}	🟩	🟩	🟩	🟩
{NO_3, HO_2}	🟥	🟥	🟥	🟩
{NO_3, HO_2, sol}	🟩	🟩	🟩	🟩
{NO}	🟩	🟩	🟩	🟩
{NO, NO_3}	🟩	🟥	🟥	🟩
{OH}	🟩	🟩	🟩	🟩

Pathway	Default values	NO = 5 ppb, NO_2 = 2 ppb	NO = 5 ppb, NO_2 = 5 ppb	OH = 10^{-3} ppb
{OH, HO_2}	🟩	🟩	🟩	🟥
{OH, NO_3}	🟩	🟩	🟩	🟥
{OH, NO_3, sol}	🟩	🟩	🟩	🟥
{OH, NO}	🟩	🟩	🟩	🟩
{OH, NO, NO_3}	🟩	🟥	🟥	🟥
{NO, NO_2, NO_3}	🟥	🟥	🟩	🟥
{NO, HO_2}	🟥	🟥	🟥	🟩

Default values:

OH (ppb) = [10^{-6},10^{-4}],
NO (ppb) = [1.17 x 10^{-6},5.32 x 10^{-1}]
NO_2 (ppb) = [1.01 x 10^{-4},1.01 x 10^{-2}],
NO_3 (ppb) = [2.3 x 10^{-4},2 x 10^{-2}],
HO_2 (ppb) = [4.15 x 10^{-2},0.5],
O_3 (ppb) = [16.7,100],
CH3OO (ppb) = [0.1,0.2],
Sol (unitless) = 0.,1]”

Comment 4:

The authors seem neither to explore nor to be aware that by neglecting most intermediate species (which deposit on surfaces, react in aqueous media and are transported away) any 3D-model would commit an error in the predictions of the priority species. I think this aspect should be discussed or at least mentioned.?

The reviewer raises an interesting point that will be true of any reduced mechanism. We note that heterogeneous and multiphase chemistry of IEPOX, IPN, and IPC is considered in CRACCM-AMORE. We expect that organic nitrates are the most important gas-phase isoprene-derived compounds for the accurate modeling of deposition. Organic nitrates are relatively well-represented in the AMORE Isoprene 1.0 mechanism, representing 4 out of 12 of the species.

A description was added to section 2.4.2 to provide more detail:

"IEPOX has heterogeneous chemistry (reactive uptake leading to SOA) following Pye et al. (2013) with updates in Pye et al. (2017) and Pye et al. (2022). The first generation isoprene organic nitrate heterogeneous chemistry (leading to HNO_3 *and gas-phase alcohols) was implemented in this work and is specific to AMORE (not in base CRACMM1).*

In CMAQ, the species in AMORE undergo deposition. All species that were already present in the base CRACMM1 mechanism were treated the same as in CRACMM1. IPN and IPC were both wet deposited with Henry's law coefficients predicted by OPERA Mansouri et al. (2018). In addition, the species were dry deposited using species-specific diffusivities, mesophyll resistances, and LeBas molar volumes."

We have added a brief discussion of these processes in section 3.3 as well:

"The CMAQ implementation also included heterogeneous chemistry for IEPOX and first generation isoprene organic nitrates, and deposition for all species. These processes, while not included in our box models, did not significantly impact the overall performance of the mechanism, as OC values were similar between AMORE and the base CRACMM1 mechanism (see section S.13)."

To the extent that field data are available for model comparison, AMORE Isoprene 1.0 has met the goals of simulating isoprene chemistry, accurately simulating isoprene concentrations and eight priority products (see Section 2.2), with small mechanism size. While field data for IEPOX and other products which contribute to SOA were not available for comparison with the CMAQ modeling results, its multiphase chemistry is explicitly considered in CRACMM1-AMORE and the results from the OC bias plot (Figure S.12.c in section S.16 given here for reference) show that AMORE gives reasonable results, and does not significantly change OC concentrations from the CRACMM1 baseline. As more field data on isoprene oxidation products and intermediates become available, more testing of the impacts of these phenomena will be possible. In addition, future work will focus more directly on isoprene SOA using the AMORE mechanism over larger domains.

AMORE mechanism evaluation: OC biases