

Review of Zhang et al (2021) GMD

The article presents a comprehensive comparison of three chemistry scheme – GOCART, RACM_GOCART and RACM_SOA_VBS – against each other and observational data from the ATOm-1 flight dataset. Compared to GOCART which uses simple sulfur chemistry and aerosols and prescribed oxidants, RACM_GOCART represents an increase in the sophistication of the chemistry scheme by using the RACM chemical mechanism including interactive oxidants. The RACM_SOA_VBS scheme appears to use this more advanced chemistry and an updated SOA scheme using a VBS approach for SOA.

The authors first perform a global comparison of the GOCART and RACM_GOCART scheme for sulfate, PM_{2.5}, H₂O₂, NO₃ and OH to investigate the influence of the updated chemical mechanism. The authors highlight a large difference in sulfate aerosol between the schemes, attributing this to differences between the prescribed oxidants in GOCART and the interactive oxidants in RACM_GOCART. The global distribution of SOA simulated by the RACM_SOA_VBS scheme is also discussed.

Then all three schemes are compared to observations from ATOm-1 flights with separate sections devoted to the flight data over the Atlantic Ocean and continental United States by comparing hourly model data to high frequency flight data.

The flight over the Atlantic encounters separate regions with high biomass burning emissions, from central Africa, and dust emissions from the Sahara. Chemical (CO, O₃, OH, CO and H₂O₂), aerosol (EC, dust, sea-salt) and meteorological variables are compared. The RACM_SOA_VBS exhibits improved EC performance compared to the other two schemes, attributed to a more realistic wet deposition approach. All schemes are generally able to reproduce the latitudinal and vertical profiles of key chemical tracers although they also exhibit high bias in CO at low altitudes around the biomass burning region.

From the flight data over the United States, particular attention is paid to California and Kansas. RACM_SOA_VBS again is much better than the other schemes at high altitudes. Low altitude EC and sulfate are high biased in all schemes, attributed to discrepancies between real and simulated emissions, while the two schemes which use interactive oxidants, RACM_GOCART and RACM_SOA_VBS, are worse than GOCART with its prescribed oxidants for high altitude sulfate.

Finally, correlation analysis is performed for sea-salt aerosol in the GOCART scheme and key species produced from biomass burning. Model sea-salt is generally high biased and while the EC/CO ratios in the model and observations compare favourably, model O₃ production appears to be underpredicted. This is attributed to the uncertainty in the associated VOC emissions.

This study makes good use of observational data and presents the model-observational comparisons in a clear way for the most part. I also commend the authors' efforts to compare a wide of range of chemical, aerosol and meteorological data and highlight the link between oxidants and aerosols. However, I do not believe this paper should be published until revisions have been undertaken to the text and further investigation performed. Some of these revisions involve checking that figures are labelled correctly, sections are numbered correctly, units are provided and references to figures in the text are correct. I provide a full list of my comments below.

Section 2

2.2.1 - Given the importance of aerosol in this study, could you clarify what you mean by “bulk” aerosols for BC and OC? Does this mean that they are simulated to have as a single mode?

2.2.2

Typographical error P6 Line 5 in citation

The phrase "rate constants and product yields from the most laboratory measurements (Stockwell et al., 1997)" is unclear - do you mean that most of the rate constants and product yields are derived from Stockwell et al (1997)?

To give the reader an idea of the complexity of RACM, it would be helpful for you to state:

- the number of chemical species
- the number of reactions

Can you also provide a description of the SOA scheme so that the update in the RACM_SOA_VBS scheme is clear? Do biogenic species such as isoprene make SOA in the atmosphere?

2.2.3

It is not entirely clear how the RACM_GOCART and RACM_SOA_VBS schemes differ in their chemistry. It appears that the RACM_SOA_VBS schemes uses the RACM scheme plus the SOA_VBS but the sentence (P6, line 16-18):

"The RACM_SOA_VBS scheme includes photolysis reactions for multiple species, full nitrogen and VOC (anthropogenic and biogenic) chemistry, inorganic and organic aerosols."

differs from the description of RACM_GOCART in Section 2.2.2, leading to confusion.

If RACM_SOA_VBS does use the same chemistry, these sentences should be either made to be identical or the sentence in Section 2.2.3 removed.

As the key update in RACM_SOA_VBS is the SOA VBS scheme, a short description of the VBS approach should be added. This should include how SOA precursors are generated - i.e. prescribed or produced by oxidation of biogenic/anthropogenic species and if so, which ones. For example, in Section 2.3.4 [sic], organic condensable vapours (OCVs) are referenced in relation to the VBS but they make little sense if additional detail is not provided Section 2.2.3.

A table showing the similarities and differences between the 3 schemes should be added to aid readers. An additional column which highlights the added value of each update (e.g. relative to GOCART RACM_GOCART shows impact of improved chemistry) would be highly beneficial.

2.3.4 - this should be renumbered to 2.2.4

P6, Line 24 - missing "Model"

Section 3

General comment: Please change all time units from ".Z" to the time in UTC (e.g. 00Z to 00:00 UTC) where UTC has been defined on its first usage as Coordinated Universal Time.

Figure 2 - typographical error with units (assume micrograms/m³) although note that it is correct in caption list. Information should be provided in the caption and at the first mention of Figure 2 in the text that the simulated model data (presumably?) corresponds to the surface concentration.

The caption in Figure 2 is also confusing. You state a 120-hour forecast – does this mean you have taken an average over 5 days? Yet you also state a single time point – I do not understand how these relate.

The description of how the chemical forecasts is performed is confusing. When you say the chemical species are “cycled every 24 hours from their output”, do you mean that the final chemical state of the previous day is used to initialise the chemical state of the model for the next day?

P8, Line 39 onwards - The statement that concentrations in excess of 100 micrograms/m³ are simulated in "wide areas of south Africa, areas of south Asia and eastern China" should be reconsidered. Concentration > 100 micrograms/m³ are only simulated in small part of these regions.

P9, Line 1 - concentration should have units of 100 micrograms/m³

P9, Line 5 - it is said that sulfate is not shown yet Fig 2 (d-f) are described as plots of sulfate. This needs to be clarified. If the intention is to show the sulfate, then it does appear that there is a good spatial correlation between the regions of lower PM_{2.5} in RACM_GOCART and regions of lower sulfate.

"We find the reductions of sulfate are about 10 µg/m³ on the order of 40-80% over the eastern US and are up to 40% over eastern China in RACM_GOCART (Fig. 2b)."

While this statement appears acceptable for China, the part about the eastern US is confusing. Does this mean that a reduction of 10 µg/m³ corresponds to a 40-80% reduction in sulfate or the 10 µg/m³ reduction occurs over 40-80% of the eastern US?

No information about units is given for Figure 3 in the text or caption. Units of ppb is given the caption list but I doubt this is correct for some of the species, particularly for OH. It should also be stated if these are surface concentrations.

Given the acknowledged importance of OH in production of sulfate aerosol, the same analysis as presented in Figure 3 for 12:00 UTC should be presented, i.e. when OH concentrations over South America, Africa, Europe and a large part of Asia are non-negligible.

P9 Line 25-26. "The general spatial distributions are comparable to the satellite observation." This statement is vague and not supported by observational data in the study. Basic comparison to a readily available satellite product or observational data for some of the key urban areas (e.g TOAR dataset) should be made if this statement is to be retained. I am also surprised by the low (<30 ppb) O₃ over China and India.

Figure 4's caption needs to be amended to include the units and clarify the data corresponds to surface O₃ (I acknowledge that the units are given the caption list). The caption also has the same issue with confusion surrounding the use of the "120-hour forecast" and single time point – please clarify. (Same for Figure 5)

While the general SOA distribution looks reasonable in Figure 5, it is hard to understand the impact of the VBS update in the RACM_VBS_SOA scheme without seeing a comparison to SOA from the RACM_GOCART scheme. Either comparison to that or to observation should be performed to provide context for these results. Can you provide an explanation as to why SOA over the Amazon, the largest global source of isoprene and monoterpenes, is lower than SOA over the Mediterranean sea?

Section 4

Section 4.1

P10 line 22 and throughout, EC is not defined - may mean elemental carbon or organic carbon and its relationship to BC should be made clear

P10, Line 23 - which model? You should differentiate between RACM_GOCART and RACM_SOA_VBS to say explicitly that the RACM_GOCART performs well at low altitudes but it high biased at high altitudes while the RACM_SOA_VBS approach performs better.

I do not agree that the latitude-height profiles are captured "very well". For the RACM_GOCART and RACM_SOA_VBS schemes there is roughly a 100 ppb high bias in the lowest 2 km in the tropics and this should be made much clearer. I acknowledge you state there is a low bias above ~ 6 km which is a fair statement but the sentence you mention this in is confusing to read. I would suggest you split it in up into two sentences which deal with the high altitude and low altitude sections separately.

The vertical profiles of the two mechanisms are similar and, as they have the same chemistry scheme, this bias could be a result of the chemistry, vertical transport and/or emissions. Your suggestion regarding biomass burning injection height appears sensible. Can you provide any additional information show where the BB emissions are injected? Given that tropical CO is high biased from the surface, could it be that the BB emissions are added at the surface?

It is interesting that O₃ is well modelled at the surface despite the high CO bias, and it could be the case that the mechanisms are getting the right answer for the wrong reasons (i.e. O₃ is good because CO is too high). It would be instructive to add the observed and modelled NO₂ concentrations, if available, as this would provide further information about the injection height of BB emissions and ozone production efficiency of the mechanisms.

P12, Line 4 - do you mean the biomass burning, in which case it would be Figure 9(a) or dust and so Figure 9(b).

Looking at Figure 9, the injection height of the BB emissions could be an issue and, as mentioned previously, I think it would be useful to see the NO₂ concentrations because if these are quite similar between mechanisms and observations, it would solidify the claim that the mechanisms reproduce O₃ well. In addition, if there are any observations of other biomass burning tracers such as acetonitrile (I assume this is not a tracer in the model), this would also be useful to plot since it would provide some information about where the biomass burning emissions are actually reaching up to.

Section 4.2

Section 4.2 P12 Line 31 please change anthroponic to anthropogenic

Your suggestion of model emissions being high biased seems reasonable. However, I would like to see a short run where BC and sulfate emissions are scaled by 0.5 to test whether this is indeed a major driver of the model high bias. If this leads to improved model performance, it would strengthen the argument that the simulated chemistry is doing a good job.

It is interesting to note that the GOCART scheme, which uses prescribed H₂O₂, OH and NO₃, performs better for high altitude sulfate. However, given your suggestions regarding the possible high bias of model emissions, it is not clear whether the GOCART prescribed oxidants approach is getting the right answer for the wrong reasons. This makes conducting a 0.5x scaling test even more important. The profiles of CO, HCHO and O₃ from the 0.5x scaling should also be discussed since you suggest the emissions bias may affect them too.

It would also be helpful to show how prescribed oxidants used in GOCART compare to observations and the oxidants simulated by the RACM_GOCART and RACM_SOA_VBS since this would provide further information as to the drivers of the sulfate high/low bias. For example, if the prescribed oxidants are lower than those in RACM_GOCART and RACM_SOA_VBS oxidants, it could explain the lower sulfate production and concentrations.

Section 6

Page 14 line 16 - The sentence starting "Compared with the .." should be restructured. The GOCART scheme is the simplest mechanism considered here and therefore should be the baseline for comparisons while here the RACM_GOCART is the base for comparison. Furthermore, the next sentence flips to have the RACM_GOCART scheme as the default scheme for comparison. Please be consistent and compare RACM_GOCART to GOCART in each.

I would like to see greater structure to the conclusion, mirroring the structure of the main paper. You start with the global analysis which is fine, but this should be clearly signposted before each observational comparison - Atlantic, California and Kansas - are introduced in separate paragraphs with the final paragraph on the sea-salt and BB comparisons.

Further to my previous comments on Section 4, please highlight the issue with tropical high biased CO at low altitude where you highlight the low bias above this point. You could also retract the statement that EC is "very good" with the GOCART and RACM_GOCART mechanisms, particularly as you go on to discuss how it is improved in the RACM_SOA_VBS mechanism. I think it would be fair to say that the

EC is simulated well by GOCART and RACM_GOCART mechanisms up to 4 km but above this the mechanisms are high biased.

Further to the comment about BB emission injection height, a comment should be included regarding the NO₂ profiles.

Please change CH₂O to HCHO for consistency.

Again, while the model anthropogenic emissions over California may drive the model bias for CO etc., the results of the 0.5x scaling tests should be incorporated into the conclusion. Please also note the high bias over ~ 3km for sulfate with the RACM_GOCART and RAC_SOA_VBS schemes over the USA when you mention GOCART's good performance.