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Interactive comment on "Improvements of organic aerosol representations and their effects in large-scale atmospheric models" *by* H. Tost and K. J. Pringle

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Reply to reviewer 2 of our manuscript:
Improvements of organic aerosol representations and their effects in large-scale atmospheric models
by H. Tost and K. J. Pringle

The manuscript presents a modeling study which calculates the O:C ratio of organic aerosols based on the aging time against OH oxidation in a CPU-efficient way, suitable for large-scale modeling. The authors study the importance of different chemical aging parameterizations and compare them with the default no-

aging version of their model. They also construct a "best guess" (BG) scenario for emissions distribution based on their oxidation state and use that as a reference. The paper is generally well written and I suggest publication to ACP after addressing the comments/concerns outlined below.

We thank the reviewer for his positive statement and and his efforts to clarify the special points mentioned below. In a revised manuscript version these aspects will be reformulated to avoid misunderstandings.

In general, I do not understand why the authors decided that the hydrophobic aerosols cannot oxidize. They are less oxygenated, thus they should have higher vapor pressure and even probably some unsaturated bonds, making them susceptible to volatilization and oxidation. I see no reason why their BG simulation is not the "Insol" one.

We agree with the reviewer that also the hydrophobic material should be able to be oxidised as in the "Insol" simulation. However, this simulation showed a substantial difference in the atmospheric burden compared to the other model configurations. Since the comparison with observations presented in Pringle et al. (2010) showed a relatively good agreement, this would be considerably disturbed by the ageing process. Consequently, the good agreement can potentially result from compensating errors, i.e. the chemical and microphysical ageing compete for the hydrophobic material. Furthermore, in our simplified approach we assumed the oxidised hydrophobic material to be converted into hydrophilic OC: in reality that is not always the case such that our "Insol" configuration overestimates the conversion from hydrophobic to hydrophilic material. Based on these two considerations we decided for a more conservative approach, and used another scenario as best guess, in which a reasonable agreement with O:C ratios with observations has been obtained.

The discussion is overly qualitative. When comparing different simulations the authors should try to make it more quantitative, when possible.

In the revised manuscript we will be more quantitative, putting the numbers of the graphs into the text, such that the reader can see more directly the magnitude of the effects and differences.

There are two “kinds” of agings in this study: one is the chemical one, and one is the microphysical one. Not everywhere it is clear which process is implied. Care must be taken throughout the manuscript, and especially in section 2.2, to clarify this every time aging is mentioned.

The reviewer is right, that both ageing processes are included in the model configuration. Hence, we will be more careful throughout the manuscript to mention which ageing is meant. The simulation setup section will be slightly extended to address the individual ageing process in the simulations in detail.

Specific comments:

Abstract, lines 20-22: I do not understand this sentence at all.

The sentence has been badly formulated and will be modified. We wanted to state that taking the O:C ratio into account an additional information of the aerosol state can be used to estimate the water uptake by organic material into the aerosol particle. This corresponds to a physically or chemically more consistent (and therefore better) description of the water uptake. Since we don’t compare the organic aerosol water uptake with experimental data to underline the improvement, we cannot make any statement whether this is really a better representation.

Page 10333, lines 9 and 22: It is not true that most models have only one tracer. The simplest models have at least two tracers, in order to parameterize fresh and aged organic aerosols.

We agree that models tend to treat organic carbon in hydrophobic and hydrophilic states, but most global models are not able to distinguish between a hydrophilic OC particle being in the atmosphere for 1 hour and one being airborne for 1 week. In

our statement we also spoke about global aerosol models, in which such a distinction is usually not done. Some more sophisticated models for SOA formation use more compounds if the SOA is explicitly treated. However, for the microphysical properties often the SOA compounds are lumped together as one OC compound loosing the identity and history.

Page 10334, lines 9-12: This assumption, although clearly stated throughout the manuscript when needed, might not necessarily be true for all cases around the globe. In fact, the authors do mention it later (end of page 10351). A statement is needed that quantifies how much this assumption will affect the results, and, more importantly, whether it will modify the conclusions. If needed, an additional simulation can be helpful.

We agree that this is the basic assumption of the manuscript. Based on the available data we simply made use of the assumption and tested its implications. Of course, the absolute value in the relation between O:C and kappa would be different, but nevertheless other fitting functions would lead to qualitatively similar results, since an increase of hygroscopicity and hence water uptake is obvious for all selected data. Of course a change in the relation would impact the organic aerosol kappa and the climate relevant parameters. However, since the effects on these quantities are anyhow low we do not expect dramatic changes. Nevertheless, we will slightly expand the discussion.

Page 10334, last line: I do not understand what this means.

We will reformulate this section. We intended to state that the two kappa values for aged and non-aged organic aerosol as proposed by Chang et al. (2010) do not show a spectrum of kappa values for different O:C ratios, whereas our approach at least provides kappa values for the intermediately aged components. As seen from Sect. 3 in the supplement of our manuscript the age spectrum of the organic aerosol is not distinct to only the lower and upper end of the spectrum, but also the intermediate ageing categories are similar important. Furthermore, the geographic location also shows substantial influence caused by the available OH concentrations.

Page 10337, top: how can hydrophobic material go in the cloud? It is only partly hydrophobic? Also, what is the bulk sea salt?

Small hydrophobic particles can undergo nucleation scavenging based on the brownian motion with cloud droplets; hence they don't activate but "coagulate" with existing cloud droplets. This process can be of relevance for the high number concentration of hydrophobic aitken mode particles due to their relatively small size, but it negligible for large particles. Activation of hydrophobic particles is forbidden in the model. However, coated material still can activate since it is transferred into the hydrophilic modes, i.e. coated mineral dust or black carbon is able to activate. Bulk seasalt is everything that is not defined as sodium, chloride and sulphate, i.e. magnesium, calcium, brominde, carbonates, etc. This fraction is small compared to the fractions of sodium and chloride and also smaller than sea salt sulphate.

Page 10338, line 5: OH is not abundant, it is only extremely reactive, which is why it is so important.

We agree, the formulation was not well chosen, but due to its high reactivity it is relevant; this will be reformulated.

Page 10339, line 3: The approach described here is very old and is being abandoned fast by global climate models. It should not be mentioned here as the current standard, but rather as an obsolete parameterization that should be eliminated.

In this aspect we disagree; regarding the AEROCOM experiments a lot of current global state of the art models use this approach to describe secondary organic aerosol emissions, based on fixed fractions of terpene and isoprene emissions. We agree, that this approach should be eliminated quickly from models, but unfortunately it is likely that this is going to last for at least a few more years.

Section 2.1.2 needs great expansion; it is extremely short for the importance it has and the discussion that follows. The reader needs to know more about the processes described here. In addition, although it is obvious that it will make the model more computationally expensive, it is not clear why it is suitable for "process research rather than long-term climate studies". A reference or some explanation is needed here. The last sentence of the section is also confusing: is this process included or not in the current study? Aqueous SO2 oxidation is very important, is it included in the simulations or not?

We will elaborate more on the model description of this part in the revised manuscript. The applicability restriction is simply based on the computational costs; the code for the non-equilibrium chemistry in the aerosol phase increases the computational costs by up to 20The distinction between aqueous phase, aerosol and cloud phase will be made more obvious in the revised manuscript. The SO2 oxidation in the aqueous cloud phase is included in all simulations. However, our studies have shown that the SO2 oxidation in the aerosol phase is less than 3

Page 10341, lines 11-13: these add to 50%, where is the rest half?

The total hydrophilic SOA emission flux is separated: 50% are emitted into the aitken mode and 50% into the accumulation mode. Consequently, the separation into the WSOC compounds require to sum up to 50% of the total hydrophilic SOA emission flux per size category as well.

Page 10341, lines 15-16: the marine organics are first mentioned here. The reader knows nothing about them, how they are being produced, what they are, what are their properties, their mixing state with other aerosols, etc. They are being used later in the discussion, thus a description of them is needed somewhere in the model description sections.

The marine biogenic emissions are mentioned in the general model description (page 10337, line 16) following Vignati et al.(2010) . We will describe this emission parameterisation a little bit more in detail: they are emitted as internally mixed particles together with sea salt, but restricted to the submicron range.

Page 10341, point 5: This aging happens via which mechanism? Same as the hydrophilic one? At what rate?

In this simulation the chemical ageing is done in the same way as in the other simulations for the hydrophilic material. The main difference is that the resulting oxidised material is assumed to be more hydrophilic, i.e. OC from the hydrophobic mode is assumed to be converted to one of the WSOC compounds of the hydrophilic mode. This also means that the WSOC compounds do not exist in the hydrophobic modes. Consequently, this conversion from hydrophobic to hydrophilic modes operates on the same time scales as the oxidation, hence much faster than typical microphysical conversion via coating or coagulation in case of sufficient OH concentrations.

Page 10345, line 15: no need to believe that the other model is correct. “accurate” should be used with caution, maybe “similarly” is a better word.

This will be reformulated. We used the other model as a reference here, but we agree that the model does not necessarily represent reality. However, the flight data show a relatively similar pattern, such that we believe that the gradient is represented with acceptable accuracy by both models.

Page 10345, lines 20-22: This should also be mentioned in the figure legend. Page 10346, lines 5-6: I do not see a similar tendency in the model results, they are rather flat, compared to the measurements that show up to a factor of 2 differences.

This will be added. We will replace this figure by one using the correct season for all data points; however, the correct meteorology will not be simulated such that the comparison is still a bit more qualitative, since the observations originate from several years. This figure as well as the time series for all data points will be moved to the

supplement. Consequently, the text passages in this section are going to be modified as well. Overall, the data for summer time are reproduced relatively well by the model, whereas the winter time data is mostly underestimated by the model. This shows the importance of the OH concentrations dominating the ageing and therefore the O:C ratios. In winter time with low O:C ratios the ageing is slower and hence lower O:C ratios are simulated whereas for some stations even higher oxidation states are observed. This can result from different kinds of emissions during winter, e.g. local heating in remote areas versus industrial emissions transported to remote regions. Also the oxidation state of the primary emissions might have been underestimated, since during summer time the biogenic emissions with a higher O:C ratio at emissions have a more dominant influence on the total O:C ratio. This will be discussed in the revised manuscript.

Page 10347, lines 1-6: how can you perform statistics with just a single year of simulations? The 12 data points of the monthly means are not good numbers to be used to compare 2 annual means, due to the strong seasonality. The correct way to do it is to have 5 or 10 years of simulations and compare the 5 or 10 annual mean numbers of a simulation with the corresponding data of another simulation.

We did the statistics on the model output of 5 hourly intervals. Consequently, we get a full diurnal cycle within 5 days and obtain more than 1700 data points for one year. The two data sets from two simulations are therefore subject to the same diurnal and seasonal cycle such that this should not be a limitation as well. In fact the different ageing potential in the different seasons, and its feedback on other chemical compounds is one of the aspects of investigation for our study. Since the meteorological conditions are identical in all simulations, (achieved by suppressing all feedback between chemistry, aerosols, clouds and radiation) the differences in the simulations do not originate from transport, weather or similar phenomena, but only from the chemistry. Overall, the statistics used here are provided as a mean to make sure that the obtained differences between the simulations are not random, but can be related with a high significance to the underlying processes. If feedback would be allowed, we agree that the approach of the reviewer is the correct one, e.g. to analyse the climate impact of the ageing representation via the direct and indirect aerosol effects, but this is beyond the scope of this study.

Page 10347, line 8: I wouldn't use "storm tracks", since this implies that storms are related with (or, they are responsible for) the low values. In case they are, this has to be shown.

The regions of the midlatitude storm tracks are well defined in a meteorological sense. Since especially over the Southern ocean the low oxidation capacity of the atmosphere, but also the primary emitted organics from marine sources caused by the high wind speeds, there is even a causal relationship. Nevertheless, this can be rephrased.

Page 10348, second half: It would be interesting to calculate the mean time that takes for the changes to not be important at all. This will show how far downwind of sources the emissions assumption is unimportant.

As in our study, we have no passive tracer or marker to calculate the contribution of a dedicated source; this is hardly possible with the current model configuration or existing data sets. Using non-mixing box trajectory models might be helpful with that aspect. However, since the O:C ratio at all locations always is caused by a mixture of several components, i.e. one can find an unlimited number of linear combinations to come to the same result, this is difficult to determine properly. This analysis goes beyond the scope of the current study, but we agree that with the help of tagged aerosols, passive tracers or similar approaches this might prove an interesting result and worth continuing studies.

Page 10352. Line 7: "less efficient" compared to what?

The lower efficiency is compared to the "No-Ageing" simulation in which kappa$_{org}$ is assumed to be constant with a value of 0.1. This will be made clear in the revised manuscript.

Section 3.3: How about aerosol size? What fraction of water per size is due to organ- ics? How about the fraction at CCN sizes?

The aerosol dry size is influenced to a minor degree, whereas the ambient aerosol size is influenced by the amount of organic aerosol water. The upper right panel in Fig.6 shows the contribution of total organic water as a column quantity. The size resolved organic aerosol water columns will be added to the supplement and discussed shortly in the manuscript. Since the CCN are calculated from the dry aerosol spectrum, the same statement as mentioned above is valid here as well. We will also add the contributions of the CCN per size category in the supplement and discuss it briefly.

Page 10360, lines 15-20: Does this change improve results when compared with measurements, or not?

This change results in an underestimation of OC compared to the base case at most stations of the IMPROVE network. This was one of the reasons why the "Insol" simulation did not become our "best guess". This will be made clear in the revised version.

Page 10360, lines 24-25: If you are referring to figure 4, I disagree. There is no reasonable agreement. Figure 4: This is a very interesting figure and well explained in the text. I suggest trying to find the temporal information from Ng et al. and plot it with the appropriate model data, not the annual means. I have the feeling that this might improve the comparison with measurements.

We agree that there are some deficiencies in the model representation especially for the highly oxised data samples. Based on the request of the reviewer this figure will be replaced by the one using the correct dates with respect to the simulation days. Still the deficiencies partly remain, but we can deduce them further to winter times with low oxidation capacity in the model, which will be mentioned in the conclusions as well.

Technical aspects: We will carefully check the whole manuscript for sentences with potentially confusing statements and recheck the spelling.

Page 10334, line 4: Donahue et al. (2006) does not mention 2D VBS.

We agree, this citation slipped from the part above, it will be moved to the section introducing the VBS.

Figure 2: what are the symbols “k”, “s”, etc.?

The symbols in Fig.2 will be explained in more detail in the figure caption, as also requested by the other reviewer.

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