

Interactive comment on “Change in global aerosol composition since preindustrial times” by K. Tsigaridis et al.

K. Tsigaridis et al.

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We would like to thank the reviewer for his comments, since his recommendations contribute to clarify specific aspects of the manuscript. His/hers consideration have been taken into account for the revised version of the paper. We provide below the answers to the specific comments made.

(1) This manuscript is not the only study on aerosol chemical composition changes since preindustrial times considering SOA with all other main aerosol components. In particular, LiaoSeinfeld05 studied the change in global distribution and radiative forcing of sulfate, ammonium, nitrate, BC, POA, and SOA from preindustrial period to 2100 using a unified chemistry-aerosol-climate model. Mineral dust and sea salt were also included in that study (global burdens were reported in Liaoetal04). This manuscript should cite LiaoSeinfeld05 and compare the results of this study with those of LiaoSe-

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infeld05.

Reply: We have corrected this part, both in the abstract and the text, as requested also by the second reviewer. The calculated burdens of aerosol components from Liao and Seinfeld (2005) have been included in the Table 5 of the manuscript and a burden comparison has been included in the last paragraph of section 3.2. A more detailed comparison has not been made, since Liao and Seinfeld (2005) discuss the impact of heterogeneous reactions on aerosol and ozone radiative forcing, while our work focuses on the change of aerosol composition.

(2) Even though much of the model details of this study was provided in TsigaridisKanakidou03, more details should still be provided in this manuscript to make this manuscript more self-contained. Examples of things that need to be addressed include: What is the gas-phase mechanism used? What is the model time step? How are emissions of monoterpenes and ORVOCs speciated between α -pinene and β -pinene? What percentages of emitted BC and POA are assumed to be hydrophobic?

Reply: The description of the model has been extended to provide all the information requested by the reviewer (Section 2, 3rd paragraph; Section 2.1, 1st paragraph).

(3) Does the model used for the current study consider SOA formation from further oxidation of the higher volatility products shown in Equation 1 as in TsigaridisKanakidou03? To which simulation scenario of TsigaridisKanakidou03 does the SOA model used in this study correspond? The manuscript should provide more detailed discussion of differences (model and results) between this study and TsigaridisKanakidou03. What is the preindustrial and present-day annual global SOA production rates determined by this study?

Reply: The model does not take into account further oxidation of the primary oxidation products. Further, our scenario does not correspond to any of the sensitivity scenarios described by Tsigaridis and Kanakidou (2003). This is now mentioned in the text: "Although Tsigaridis and Kanakidou (2003) have shown that the oxidation of SOA com-

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ponents can increase the SOA production by about 20%, in the present study the SOA components are assumed to be chemically inert, since the parameterization is based on overall yields of SOA formation from chamber experiments. More detailed information of the base scenario used in this study is described in Tsigaridis et al. (2005).” Both articles are available on the ACP website.

(4) The manuscript is not clear on how the dependence of SOA yield parameters on VOC:NO_x is modeled. There are three sets of SOA yield parameters for a-pinene. What values of VOC:NO_x ratio are considered high VOC:NO_x conditions? At what range of VOC:NO_x ratio do APIN_p1H and APIN_p2H form? How about APIN_p1 & APIN_p2 and APIN_p1N & APIN_p2N? Modeling of SOA yield dependence on VOC:NO_x is very new. How sensitive are the model results to this dependence?

Reply: As the reviewer requested, we have extended the explanation of the consideration of the VOC:NO_x influence on SOA formation in the model. We also added Figure 1 that illustrates clearly the high and low VOC:NO_x regions, and commented on the importance of including such a parameterization in a global model (Section 2.3).

(5) For SOA modeling, this study categorizes the biogenic monoterpene and ORVOC emissions into a-pinene and b-pinene. Because of the uncertainties involved in SOA yields and computational efficiency, classifying SOA precursors into groups is in general a good idea. However, the manuscript does not explain why a-pinene and b-pinene were chosen as surrogates and current understanding of SOA formation suggests that more categories are needed to properly represent the wide range of SOA yield parameters. For example, sesquiterpenes generally have higher SOA yield than monoterpenes Griffinetal99b. Also, Ngetal06 suggest that the number of double bonds in the parent VOC determines whether SOA formation is rate-limited by the first oxidation or later oxidation steps.

Reply: We clearly agree with the reviewer that different types of compounds have different aerosol yields. However, increasing the number of the species in a global model

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is very expensive computationally. The α - and β -pinene species are most widely used as surrogates (in some studies, α -pinene alone) due to their high abundance compared to the other biogenic VOC (excluding isoprene) on a global scale. Considering the number of double bonds, the experimentally-retrieved aerosol formation parameters from chamber studies should include both first and second generation products, at least the experiments that lasted several hours. Additionally, the consideration of oxidation of primary products in the gas-phase is now discussed (see answer to point 3; Tsigaridis and Kanakidou, 2003).

(6) It has been determined that products of isoprene oxidation also lead to SOA formation (e.g. Claeys et al., 2004; Kroll et al., 2005; Kroll et al., 2006). Henze and Seinfeld (2006) indicate that including isoprene as a source of SOA causes substantial increases in predicted SOA concentrations, particularly in the free troposphere and remote marine environments. How would inclusion of isoprene oxidation as a source of SOA affect the results of this study?

Reply: Indeed, isoprene is a precursor of SOA. For the present study we used the simplified approach of 0.2% molar aerosol yield from isoprene oxidation (Claeys et al., 2004). This approach does not make isoprene a substantial aerosol precursor and will be improved in future studies, based on Henze and Seinfeld (2006) recommendations. We have added this comment in the manuscript, in the introduction of section 2.

(7) This study assumes that conversion of hydrophobic BC and POA to hydrophilic BC and POA is determined by ozone oxidation and that the globally averaged turnover time is approximately 1 day. How does this turnover time vary geographically and vertically? The value of 1 day is most likely an upper bound estimate because condensation of hygroscopic material such as sulfuric acid can also convert hydrophobic aerosol to hydrophilic aerosol. Looking at functional groups using scanning transmission x-ray microscopy, Maria et al. (2004) estimated the oxidation rate is approximately 24% per day for BC and 13–21% per day for OC; these values correspond to turnover time of about 5 days. Can the authors provide insights as to why the modeled turnover time is much

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smaller?

Reply: The temporal and spatial distribution of the hydrophobic-to-hydrophilic carbonaceous aerosols has been described in detail in Tsigaridis and Kanakidou (2003). A figure has already been provided there (Figure 2 in that paper that is available on the web) and the associated uncertainties have been discussed. As shown in that figure, the conversion time displays large spatial and temporal variability (from hours to several days) since it depends on ozone and relative humidity levels. The experimentally derived turnover times of hydrophobic to hydrophilic aerosol reported by Maria et al. (Science, 2004) agree reasonably well with the estimates by Tsigaridis and Kanakidou (ACP, 2003) (Figure 2) when taking into account the season and the area of the observations.

On the other hand, adopting a globally mean turnover time of 5 days in the model close to these observations would lead to unrealistically high aerosol burdens. As mentioned also in point 6 of our replies to reviewer #2, on a global and year around basis, the tropospheric lifetime of hydrophobic aerosols in our model is similar with the turnover times proposed by Cooke et al. (1999) and used by most global modelers. Assuming that ageing occurs by sulfuric acid condensation requires internally mixed aerosols, while in our study aerosols are considered externally mixed. We consider that having a spatially and temporally variable turnover time of hydrophobic to hydrophilic aerosol driven by chemistry rather than a constant value is an improvement compared to earlier studies with externally mixed aerosols.

(8) Since the modeled aerosol optical depth is derived from aerosol composition and size, the section “Aerosol optical depth” should be placed after section “Aerosol Composition”.

Reply: The section on AOD is now at the end of the discussion (3.5). The corresponding change in order is made also in the conclusions.

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