P2.5 A modeling study of secondary organic aerosols using a general circulation model

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1. Introduction

Organic carbon aerosols are generally divided into two categories by formation processes: (1) Primary organic aerosols (POA) are emitted directly in form of particles by biomass burning, fossil fuel combustion, and various combustions. (2) Secondary organic aerosols (SOA) are produced in the atmosphere by photo-oxidation of volatile organic compounds (VOC) followed by partitioning or condensation of low volatile products into the aerosol phase. These VOC include both natural VOC such as terpenes and anthropogenic VOC such as toluene and xylene.

The natural SOA is important for two aspects: (1) the SOA that is major background aerosol in especially the tropics is needed for estimating aerosol radiative forcing due to human activities from industrial period, (2) the SOA formation in the tropics is strongly linked through ozone formation, which chiefly determines the level of ozone concentrations in the tropics.

In general, the SOA is not treated or treated very simply in mostly general circulation model (GCM) [e.g. Lohmann et al., 2000; Chin et al. 2002; Takemura et al., 2000, 2002, 2005]. This reason is mainly two: (1) SOA and even organic carbon aerosols are very complex, have many compounds and exist in various mixing state. They are unclear and uncertain. So, it is difficult to representing, expressing and modeling organic carbon aerosols. (2) In the amount of burden and emission, SOA is assumed to be much less than POA. Most GCM including tracers of tropospheric aerosols are hardly considered an SOA tracer. In fact, there are a few SOA simulation model in level of the globe and the global SOA estimation is different and uncertain by each model [Table1]. The SOA precursors in these SOA models adopt monoterpenes and other organic VOC (ORVOC) originated by Guenther et al. (1995). Recently it found that isoprene is a new precursor of SOA [Cleay et al., 2004a, 2004b; Schlolnik et al., 2005]. However, because the SOA formed through isoprene is unclear and the mechanism is uncertain, the SOA model including an isoprene as SOA precursor has never existed. The SOA formation scheme are mainly divided into two scheme; (1) based on partitioning theory [Griffin et al., 1999b] and (2) chemical reaction model by considering immediate products [e.g. Jenkin, 2004]. Generally these models simulate only SOA mass concentrations and especially direct effect of SOA. But so far the SOA indirect effect has never estimated.

In this study, we extended a global aerosol transport-radiation model coupled to a general circulation model, SPRINTARS, which simulates mass concentrations and optical properties of tropospheric aerosols (dust, sea-salt, organic carbon, black carbon, and sulfate aerosol) [Takemura et al., 2000, 2002, 2005]. In the SPRINTARS organic carbon aerosols consist of both POA and SOA and the SOA formation process is not considered in this model but given by a conversion rate of biogenic terpene depending on only seasonal terpene emission distribution of Guenther et al. (1995). But this simple parameterization in Takemura et al. (2005) is inadequate because the SOA formation depends on not only VOC concentrations but also oxidants and ore-existed organic aerosol concentrations, according to many chamber experiments [e.g. Grinffin et al., 1999b]. In this paper we considered these experimental dependences of SOA formation.

In Takemura et al. (2005), for the sake of the estimation of aerosol indirect effect they simulated cloud droplet effective radius near the top of water clouds, which reflect on cloud

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radiative properties and determine cloud albedo. Simulations of cloud droplet effective radius through this scheme as Takemura et al. (2005) in this study and comparisons to Takemura et al. (2005) lead to an estimation of SOA indirect effect, which is the first estimation of SOA impact on cloud field.

2. Model description

In this work, we used the global three-dimensional aerosol transport-radiation model, Spectral Radiation-Transport Model for Aerosol Species (SPRINTARS), which is described in Takemura et al. (2000), (2002), (2005); therefore we give only a brief description here. The SPRINTARS coupled to the Center for Climate System Research/National Institute for Environmental Studies/Frontier Research Center for Global Change (CCSR/NIES/FRCGC) atmospheric general circulation model (AGCM). The horizontal resolution of the triangular truncation is set at T42 (approximately 2.8 by 2.8 in latitude and longitude) and the vertical resolution at 20 layers (sigma levels based on the surface pressure at 0.995, 0.980, 0.950, 0.900, 0.830, 0.745, 0.650, 0.549, 0.454, 0.369, 0.295, 0.230, 0.175, 0.124, 0.085, 0.060, 0.045, 0.035, 0.025, and 0.008). The time step was set at 40 min. The model predicts mass mixing ratio of the main tropospheric aerosols, that is, carbonaceous aerosol (black carbon and organic carbon (OC)), sulfate, soil dust, and sea salt, and the precursor gases of sulfate, that is, sulfur dioxide (SO_2) and dimethylsulfide (DMS).

The aerosol transport processes include emission, advection, diffusion, sulfur chemistry, wet deposition, and gravitational settling. The radiation scheme in CCSR/NIES/FRCGC AGCM [Nakajima et al., 2000] is extended for the aerosol direct effect related to scattering and absorption by aerosol particles.

We adopted the same aerosol transport scheme as SPRINTARS except for a SOA treatment. Although in SPRINTARS they assumed SOA production was determined by natural volatile organic compound emission through simple mathematical conversion, we introduced a SOA formation scheme governed by an equilibrium partitioning of semi-volatile gases [Pankow et al., 1994a,1994b]. The semi-volatile gases formed by terpene oxidation are surrogated in two compounds for one oxidation reaction because even a single precursor terpene generally yields a large number condensable products, many of which may not have been identified in laboratory studies.

The terpene oxidation products are assumed to partition into aerosol phase due to their polarity and low vapor pressure. The equilibrium between the gas and aerosol phase of a semi-volatile products is given by

$$Gi = \frac{A_i}{K_i M_O} \qquad (1)$$

where Ai and Gi are terpene oxidation products “i” concentrations in the aerosol and gas phases, respectively. The Ki is the species “i” equilibrium constant which depends on temperature by using Clausius-Clapeyron equation [Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003]. The Mo is the total organic aerosol mass concentrations in ug/m^3 and given by

$$M_o = [OA] + \sum_i A_i \qquad (2)$$

where [OA] is the summations of the organic aerosol concentrations including POA and SOA before the current time step. The SOA concentration is calculated by solving the eq(1) and the eq(2), iteratively [Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003]. In our model, the precursors of SOA, including both terpenes and generated oxidation products, were not treated as tracers.

All the emission fluxes in the time, 1990, of aerosols and its precursor, except a precursor gas of SOA, are originated from Takemura et al. (2005). The precursor gas of SOA is only biogenic terpene, which originated from the GEIA database [Guenther et al., 1995]. The emission of biogenic terpene varies diurnally with temperature on a chemical transport model, CHASER, which can calculate the terpene oxidations with ozone and hydroxyl and nitrate radicals [Sudo et al., 2002]. Unlike other global SOA modeling study, we did not assume that other reactive VOC (ORVOCs) from biogenic compounds are not adopted as SOA precursors.

In this study, we introduced the new SOA formation and also changed the SOA dry radius. The SOA dry radius is set at 80nm, which is comparable to in situ typical measurement value, though that is done at 20nm in Takemura et al. (2005).

In estimating aerosol indirect effect, as similar to Takemura et al. (2005), we calculated cloud droplet number concentration, cloud water content, and cloud droplet effective radius for all aerosols species. A conversion of aerosol number concentrations (Na) into CCN number concentrations (Nc) is parameterized [Ghan et al., 1997; Ghan and Abdul-Razzak et al., 1998; Takemura et al., 2005]. Its parameterization (called as Na-Nc parameterization) is based on Kolher theory and is a function of updraft velocity, aerosol chemical composition, and aerosol size distribution. The updraft velocity is calculated by turbulent kinetic energy. The aerosol chemical composition reflects on solute effect in Kolher theory. The aerosol size distribution is set to be lognormal distribution function for each aerosol.

3. Result

In this section, we compared our results to observations by filed measurements in Amazon which is one of the largest areas where terpene emits and global satellite measurements.

In general, observational data for carbonaceous aerosols, especially for organic aerosol, are limited because it is difficult to measure organic aerosols for their lower concentrations and their volatilities. So far, observational data in the field we can use in order to SOA comparison were only Amazonian data.

Table2 shows both total carbonaceous aerosol mass concentrations and the total aerosol number concentrations and compares the simulation results of (1) in this work and (2) in Takemura et al. (2005) to (c) Large-scale Biosphere Atmosphere experiment in Amazon (LBA) [Desecari et al., 2005; Hoffer et al., 2005; Guron et al., 2003; Artaxo et al., 2002; Rissler et al., 2005]. We compared in only wet season because a SOA is assumed to be very minor components in the dry and transition period for the plentiful of POA emission from biomass burning.

In Takemura et al. (2005), the simulations of both the total carbonaceous aerosol and the total aerosol number concentrations in Amazon were largely overestimated because they mainly overestimated SOA mass concentrations. But in this work the modification of scheme brought better results of simulated total carbonaceous aerosol that were close to in situ observation.

Figure 1 shows the simulated SOA mass concentrations near the surface in February. As shown in Figure 1(a), (b), in most areas SOA mass concentrations in this work are lower than Takemura et al. (2005). This result was considered to reflect on SOA production dependence on POA concentrations. In fact, February is a wet season in the tropics in south-hemisphere, following that POA emissions are smaller.

Figure 2 shows cloud droplet effective radius near the top of water clouds (R_{eff}) and compares the simulation results of both Takemura et al. (2005) and this work to satellite observational data from Advanced Very High Resolution Radiometer (AVHRR) [Kawamoto et al., 2001]. The differences between these model results mainly reflect on SOA formation process. The major different areas between these model results are three areas where SOA distributed: (1) continents such as Amazon and Congo, (2) oceans such as the east Pacific near South-America, and (3) desert area such as Australia and Namibian. In the continents such as Amazon and Congo, where terpene (as SOA precursor) assumed to emit a lot, this work simulated R_{eff} larger than Takemura et al. (2005) by two or three micrometers. In the ocean, this work simulated larger R_{eff} than Takemura et al. (2005). Especially in the east Pacific area near Peru, underestimated R_{eff} in Takemura et al. (2005) was improved. The R_{eff} in these continents and these oceans areas are closer to the observational data from AVHRR and are comparable with in situ measurement values. In desert such as Australia and Namibian, this work simulated R_{eff} much larger but was far from in situ observations. This may indicate that in these areas simulated hygroscopic aerosol mass concentrations such as SOA are smaller. And this may also indicate that in these areas biogenic SOA from terpene is not major aerosol and new aerosols such as SOA from isoprene is dominant. These suggestions are our next target to understand other SOA formation processes.

4. Discussion

We discuss the relation between aerosol number concentrations (Na) and cloud droplet concentrations (Nc). It usually performs linear relationship between aerosol and CCN number concentrations, except for a condition where updraft velocity is weaker and aerosol number concentration is too higher (typically upper 2×10^5 cm^{-3}). Takemura et al. (2005) predicted that the relation in the areas such as Amazon and Congo, where SOA is large component, is a non-linear result. The reason is that their simulated SOA number concentrations are too higher in the areas. Additionally, the values were not comparable with in situ measurement ones (Table2). As a result, in this work we simulated lower SOA and higher CCN number concentrations especially in Amazon and Congo basin than Takemura et al. (2005).

The Na-Nc parameterization assumes to perform well except for a certain condition, that is, weaker updraft velocity and higher aerosol number concentrations. The function has a peak, which is a point of turning to occur in a decreasing cloud droplet number concentration as an increasing aerosol number concentration, in the range of much larger aerosol number concentration. This peak assumes to represent a competition of catching limited water vapors to each cloud droplet for their growth. A change of simulated aerosol number across the peak leads to unpredicted results of the simulated cloud droplet number concentrations. The change often occurs in the areas, where the simulated updraft velocity is weak, such as Amazon and Congo, but it is not likely to occur in the areas, where the simulated updraft velocity is relatively strong, such as the ocean near Amazon and Congo and the desert such as Australia.

5. Implications

When we estimate the aerosol direct and indirect effects due to human activities, we need to know a level of aerosol emission fluxes in pre-industrial era. The level is set at the values we assume to be right. In general, the natural SOA production assumed to be the same in pre-industrial era as that in present day [e.g. Takemura et al., 2005]. In chamber experiments, however, the natural SOA production depends on POA concentrations [e.g. Griffin et al., 1999b]. The POA concentrations in pre-industrial era assumed to be smaller than that in present day, implying that the pre-industrial level of the natural SOA production was the present level of that. Our result also shows that the smaller SOA production as POA emission is smaller (Figure3). The results have important implications for estimating the aerosol direct and indirect effect.

6. Conclusion

Compared to the simulation result in Takemura et al. (2005), which does not treat a physical-chemical SOA formation scheme, this work simulated better especially organic aerosol mass concentrations and aerosol number concentrations in Amazon area, and cloud droplet effective radius at the top of water clouds especially near SOA distributed areas, that are comparable with in situ measurement values. Additionally, in Takemura et al. (2005) a SOA production level in the pre-industrial era was assumed to be almost same as that in the present era. But this work showed that a SOA production level was lower in the pre-industrial era when the POA concentration was very small.

Simulations from this study including the physical-chemical SOA formation suggest two points in estimating influences of aerosols to radiation and cloud field: First, SOA number concentrations can determine cloud droplet effective radius near the top of water cloud in the tropics and can affect to the estimation of aerosol indirect effect. Second, disregarding POA dependence in the SOA formation process may lead to a larger underestimation of the aerosol radiative forcing because the SOA production level in the pre-industrial era generally assumed to be the same as that in present day.

7. References

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8. Illustrations and Tables

Table1. Comparison of global SOA estimation

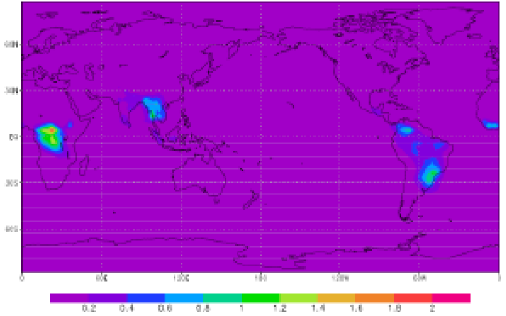
References	SOA estimation [Tg/yr]
Andreae and Crutzen (1997)	30-270
Griffin et al. (1999a)	13-24
Kanakidou et al. (2000)	61-79
IPCC-TAR (2001)	8-40
Chung and Seinfeld (2002)	11.2
Derwent et al. (2003)	63
Tsigaridis and Kanakidou (2003)	2.5-44.5 (only biogenic SOA)
Lack et al. (2004)	15.3 (partitioning method) 24.6 (bulk method)

Table2. Comparison of carbonaceous aerosol mass and total aerosol number concentrations in Amazon (10S, 62W) and in wet season (February)

(a) TW	(b) T05	(c) Obs.	references
Total carbonaceous aerosol mass concentrations			
2.50	6.79	1.3	*1
		1.6±5.6 2.0±0.6	*2
		0.8967	*3
		2.31	*4
Total aerosol number concentrations			
876	14694	890±920	*4
		1280±820 2070±1790	*5

*1 Decesari et al. (2005)
*2 Hoffer et al. (2005)
*3 Guyon et al. (2003)
*4 Artaxo et al. (2002)
*5 Rissler et al. (2005)

(a) this work



(b) Takemura et al. (2005)

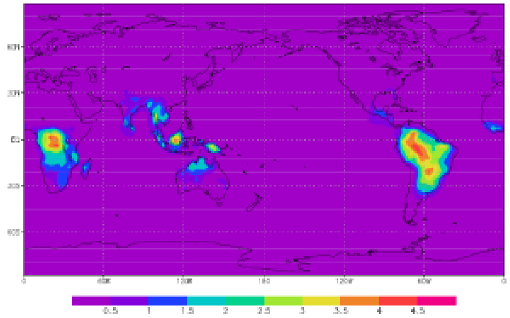
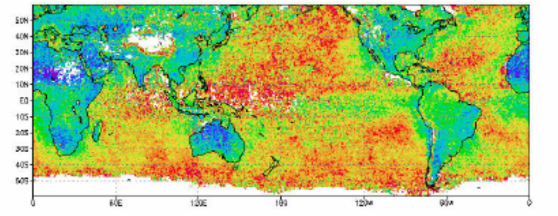
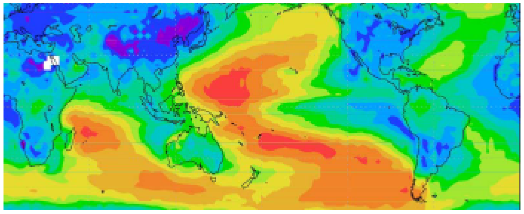


Figure1. The simulations of SOA mass concentrations near the surface, in February, [ug/m^3] by (a) this work and by (b) Takemura et al. (2005).

(a) AVHRR; Kawamoto *et al.* (2001)



(b) Takemura *et al.* (2005)



(c) This Work

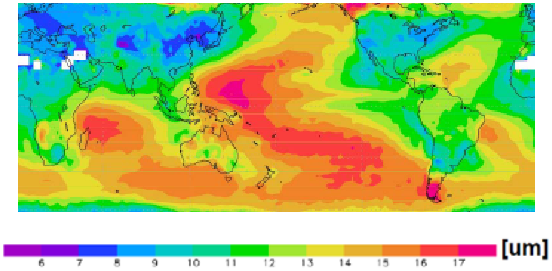


Figure2: Cloud droplet effective radius near the top of water clouds (R_{eff}), (a) satellite observation from AVHRR [Kawamoto et al. (2001)], (b) simulations by Takemura et al. (2005), and (c) simulations by this work.

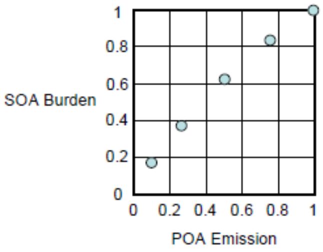


Figure3. Predicted relative SOA burden shown as a function of relative POA emission. The both value in the present day are set to equal to 1. We assumed that the relative POA emission in pre-industrial era is approximately 0.1.