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**Factors controlling  
global in cloud  
production of SOA**

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# Evaluation of factors controlling global secondary organic aerosol production from cloud processes

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## Abstract

5 Secondary organic aerosols (SOA) exert a significant influence on ambient air quality and regional climate. Recent field, laboratorial and modeling studies have confirmed that in-cloud processes contribute to a large fraction of SOA production. This study  
10 evaluates the key factors that govern the production of cloud-process SOA ( $SOA_{\text{cloud}}$ ) in a global scale based on the GFDL coupled chemistry-climate model AM3 in which full cloud chemistry is employed. The association between  $SOA_{\text{cloud}}$  production rate and six factors (i.e. liquid water content (LWC), total carbon chemical loss rate ( $TC_{\text{loss}}$ ), temperature,  $VOC/NO_x$ , OH, and  $O_3$ ) is examined. We find that LWC alone determines the  
15 spatial pattern of  $SOA_{\text{cloud}}$  production, particularly over the tropical, subtropical and temperate forest regions, and is strongly correlated with  $SOA_{\text{cloud}}$  production.  $TC_{\text{loss}}$  ranks the second and mainly represents the seasonal variability of vegetation growth. Other individual factors are essentially uncorrelated to  $SOA_{\text{cloud}}$  production. We find that the rate of  $SOA_{\text{cloud}}$  production is simultaneously determined by both LWC and  $TC_{\text{loss}}$ , but responds linearly to LWC and nonlinearly (or concavely) to  $TC_{\text{loss}}$ . A parameterization based on LWC and  $TC_{\text{loss}}$  can capture well the spatial and temporal variability of the process-based  $SOA_{\text{cloud}}$  formation ( $R^2 = 0.5$ ) and can be easily applied to global three dimensional models to represent the SOA production from cloud processes.

## 1 Introduction

20 Secondary organic aerosol (SOA) is one of the most important components of atmospheric particulate matter, which has a significant influence on atmospheric chemistry and air quality and has potential toxicological effects (Kanakidou et al., 2005). These condensable compounds are produced through physical and chemical processing of both anthropogenic and biogenic volatile organic compounds (VOCs), including xy-  
25 lene, toluene, monoterpene, and isoprene, etc. (van Donkelaar et al., 2007; Henze et al., 2008). Among these species, aromatic hydrocarbons are estimated to be the

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most important anthropogenic SOA precursors (Pandis et al., 1992), while isoprene, monoterpene, and potentially sesquiterpene oxidation products are the predominant contributors to SOA production in rural forested areas (Guenther et al., 1995; Kanakidou et al., 2005).

5 Previous global modeling studies have overwhelmingly focused on the SOA formation in the gaseous phase. However, relying on gas-phase source alone, a number of modeling results tend to underestimate SOA concentrations by a significant degree (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). In-cloud processes are found to be responsible for a substantial fraction of SOA production (Carlton et al., 10 2008; Lim et al., 2010), indicating that SOA formed through cloud processes is a strong candidate to shrink the gap between observed and model-predicted organic aerosols. For instance, laboratorial experiments have demonstrated that organic acids (e.g. oxalic acid) and oligomers can be formed from glyoxal (Carlton et al., 2007), methylglyoxal (Altieri et al., 2008; Tan et al., 2010), pyruvic acid (Carlton et al., 2006), and acetic acid (Tan et al., 2012) through aqueous-phase reactions in cloud. In addition, Ervens et al. (2004) suggested that cloud processes may act as a significant source of small dicarboxylic acids, which form SOA upon droplet evaporation. Lim et al. (2005) concluded that cloud processing of isoprene was an important contributor to SOA production.

Recent modeling studies have also shown an improved model performance when 20 cloud sources of SOA are included. For instance, Chen et al. (2007) found that when aqueous SOA production mechanisms were incorporated in the Community Multiscale Air Quality (CMAQ) model, domain-wide surface SOA predictions increased by 9%. Carlton et al. (2008) found that CMAQ model bias aloft against the observed organic carbon (OC) was reduced, when in-cloud SOA processes were included. Fu et al. (2009) predicted 11 TgCyr<sup>-1</sup> SOA produced from aqueous phase processes based on GEOS-Chem and the variability in organic aerosols was better captured. 25 Myriokefalitakis et al. (2011) found that the spatial and temporal distribution of the simulated oxalate agrees well with ambient observations at rural and remote locations when detailed aqueous-phase chemistry is employed.

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In-cloud SOA formation involves a series of complicated processes: formation of water-soluble oxidation products (via oxidation of reactive organic compounds in the gas phase), partitioning into cloud droplets, then reacting further in the liquid phase (e.g. via photochemistry, acid catalysis, and with inorganic matter) to form low-volatility compounds (e.g. organic acids, oligomers, and organosulfates), which remain either completely or partially in the particle phase upon cloud droplet evaporation (Carlton et al., 2006; Guzman et al., 2006; Perri et al., 2010). Furthermore, aqueous-phase reactions can be categorized as radical reactions and non-radical reactions. Radical reactions involve a variety of atmospheric oxidants, including OH radicals, NO<sub>3</sub> radicals, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and can be initiated by photolysis (Lim et al., 2010). Non-radical reactions include hemiacetal formation (Liggio et al., 2005b; Loeffler et al., 2006), esterification via condensation reactions (Gao et al., 2004; Surratt et al., 2006, 2007; Altieri et al., 2008), imine formation (De Haan et al., 2009a,c), anhydride formation (Gao et al., 2004), aldol condensation (Jang et al., 2002; Kalberer et al., 2004; Noziere and Cordova, 2008; Shapiro et al., 2009), and organosulfate formation (Liggio et al., 2005a; Surratt et al., 2007).

Presently only a few studies have attempted to quantitatively explore the factors that contribute to the formation of cloud SOA. For example, Ervens et al. (2008) used a cloud parcel model with explicit kinetic aqueous-phase chemistry to study the effects of initial VOC/NO<sub>x</sub> ratio, cloud PH, cloud contact time, and liquid water content (LWC) on SOA<sub>cl</sub> formation from isoprene. They found that SOA<sub>cl</sub> production was a function of LWC and cloud contact time under different VOC/NO<sub>x</sub> conditions. Liu et al. (2012) implemented a detailed cloud chemistry scheme into a climate model AM3 and evaluated the effects of cloud properties on the global SOA<sub>cl</sub> production and distribution. They found that substantial SOA<sub>cl</sub> were produced in the tropical and mid-latitude regions.

This study aims firstly to quantitatively understand the potential factors contributing significantly to the global in-cloud formation of SOA, and secondly to establish a relationship between SOA<sub>cl</sub> production and the key factors determining this process, based on the detailed aqueous-phase chemistry framework developed in Liu

et al. (2012). We describe the model and methods in Sect. 2, and then analyze the relationship between  $SOA_{\text{cloud}}$  production and factors determining in-cloud processes in Sect. 3. Results on the  $SOA_{\text{cloud}}$  parameterization and evaluation are given in Sects. 4 and 5, respectively. A variety of sensitivity tests on model parameters are shown in Sect. 6. Finally, conclusions are drawn in Sect. 7.

## 2 Method

### 2.1 Model description

This study is based on the global coupled chemistry-climate model (AM3), developed in the Geophysical Fluid Dynamics Laboratory (GFDL). The goal of AM3 is to address emerging issues in climate change, including aerosol-cloud interactions, chemistry-climate interactions, and coupling between the troposphere and stratosphere (Donner et al., 2011). The dynamical core used in AM3 follows the finite-volume algorithms described in Lin and Rood (1997) and Lin (2004). AM3 implements a finite-volume dynamical core (Lin, 2004) on a cubed sphere grid (projection of a cube onto the surface of a sphere, Putman and Lin, 2007), replacing the latitude-longitude grid used in its previous version AM2. The model is configured with a horizontal resolution of C48. The total number of grid cells associated with this study is therefore  $6 \times 48 \times 48 = 13824$ , and the size of grid cells varies from 163 km (at 6 corners of the cubed sphere) to 231 km (near the center of each face) (Donner et al., 2011). The vertical coordinate in AM3 follows Simmons and Burridge (1981), and the number of layers is 48. The uppermost level in AM3 has a pressure of 1 Pa, a height of about 86 km above the sea level. AM3 predicts both shallow cumulus clouds (Bretherton et al., 2004) and deep convective clouds (Donner, 1993), besides a prognostic scheme of large-scale cloud condensate and volume fraction (Tiedtke, 1993; Rotstayn, 1997; Rotstayn et al., 2000). A prognostic scheme for droplet number is used to simulate the interactions between aerosols and large-scale liquid clouds (Ming et al., 2007), and sulfate, organic matter, and sea salt

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aerosols are treated as cloud condensation nuclei (CCN). In AM3, gas-phase chemistry is being updated from MOZART-2 to MOZART-4 chemistry mechanisms (Horowitz et al., 2003; Emmons et al., 2010) and aqueous chemistry is based on an optimized mechanism for sulfur chemistry, merged with the updated cloud SOA chemistry (Jacob, 1986; Pandis and Seinfeld, 1989; Lim et al., 2005; Tan et al., 2009; Liu et al., 2012). The coupled mechanism includes approximately 100 gas phase species, 50 aqueous phase species, and totally 370 kinetic expressions.

Figure 1 summarizes the pathway for in-cloud production of SOA in AM3. The primary physical and chemical processes associated with SOA production include oxidation of precursors, gas-liquid transport, aqueous-phase reactions, and cloud evaporation and SOA<sub>cl</sub> formation.

### 2.1.1 Oxidation of precursors

Isoprene, terpenes, and aromatic compounds are the three representative precursors of SOA<sub>cl</sub>. Isoprene is the major organic compound emitted by plants with emission rates far exceeding those of other biogenic species. Monoterpenes (e.g.  $\alpha$ -pinene) are important biogenic VOCs emitted mainly by terrestrial vegetation and their oxidation products contribute significantly to SOA budget (Kavouras and Stephanou, 2002). Toluene is one of the most abundant aromatic compounds with average concentrations of 2–39 ppb in urban, 0.05–0.8 ppb in rural and 0.01–0.25 ppb in remote areas (Finlayson-Pitts and Pitts, 2000). These precursors are oxidized in the ambient air to form semi-volatile and low-volatile organic species as well as water-soluble gases, such as glyoxal, methylglyoxal, glycolaldehyde, acetic acid and hydroxyacetone.

### 2.1.2 Gas-liquid transport

In the presence of clouds, the water-soluble gases formed in the gas phase will diffuse into or be absorbed by the cloud droplets. The calculation of gas-liquid partitioning is

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expressed kinetically (Liu et al., 2012) and is based on the mass balance of a species associated with chemical reactions, emissions, and deposition (Lim et al., 2005).

### 2.1.3 Aqueous-phase reactions

The dissolved gases (e.g. glyoxal, methylglyoxal, hydroxyacetone, and glycolaldehyde) will be oxidized further in the cloud water through various aqueous chemical reactions, leading to the formation of lower-volatility carboxylic acid (e.g. glycolic acid, glyoxylic acid, pyruvic acid and oxalic acid). During daytime, glyoxal will react with OH radicals to form oxalic acid in cloud droplets. Remaining glyoxal upon cloud evaporation will form oligomers through acid catalyzed hemiacetal formation (Lim et al., 2010). Aqueous phase oxidation of methylglyoxal by OH radical leads to the formation of oxalic acid and high molecular weight products (Altieri et al., 2006, 2008; Carlton et al., 2006). Other oxidation products include pyruvic acid (Stefan and Bolton, 1999) and oligomer through esterification (Carlton et al., 2007). Aqueous oxidation of glycolaldehyde via OH radical can form glyoxal and glycolic acid (Perri et al., 2009). Subsequent reactions create formic acid, glyoxylic acid, oxalic acid and oligomers (Perri et al., 2009). Acetic acid oxidation by OH radical will produce glyoxylic acid, glycolic acid, and oxalic acids in the liquid phase, but no oligomers will form (Tan et al., 2012). This may be because that acetic acid only forms unstable radicals which cannot involve the subsequent radical-radical reactions to form higher molecular weight products (Tan et al., 2012). Details on multi-phase chemistry associated with SOA generation have been described by Liu et al. (2012).

### 2.1.4 Cloud evaporation and SOA<sub>cloud</sub> formation

When cloud droplets evaporate, low-volatility carboxylic acids as well as oligomers formed during cloud evaporation (Loeffler et al., 2006; De Haan et al., 2009b) are assumed to remain in the aerosol phase as SOA. Hence, the mass production of six SOA<sub>cloud</sub> species (i.e. glycolic acid, glyoxylic acid, pyruvic acid, oxalic acid, and two

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classes of oligomers formed by glyoxal and methylglyoxal) have been summed together to represent the total SOA<sub>cl</sub> mass production.

## 2.2 Model configuration

In this study, the emission inventories used for both gas and aerosol species are obtained from the database developed for IPCC AR5 studies (Lamarque et al., 2010). Sea ice cover and sea surface temperature (SST) are prescribed using databases developed at the Hadley Center (Rayner et al., 2003). Cloud droplet lifetime is set to be 30 min. Cloud droplets sizes and cloud fraction are using the model default values as described in Liu et al. (2012). Entrainment between the cloudy and non-cloudy areas is neglected here. We conduct a one-year simulation, and model outputs related to SOA<sub>cl</sub> are archived every 3 h.

## 2.3 Statistical analysis

The rate of SOA<sub>cl</sub> production ( $P_{\text{SOAcl}}$ ) is expressed as the total SOA mass formed through cloud processes in one unit time (unit:  $\text{kg m}^{-3} \text{s}^{-1}$ ). Based on physical and chemical mechanisms of in-cloud formation of SOA, the following factors are considered to mainly influence SOA<sub>cl</sub> production: LWC, temperature, the chemical loss rate of total carbon mass of primary precursors (i.e. isoprene,  $\alpha$ -pinene, and toluene), the concentration of OH and O<sub>3</sub>, and the VOC to NO<sub>x</sub> ratio (VOC/NO<sub>x</sub>).

LWC ( $\text{kg}(\text{water}) \text{kg}(\text{air})^{-1}$ ) is the media where SOA<sub>cl</sub> is produced. Temperature governs the overall reaction rates and is shown in laboratorial studies as one of the key factors in SOA formation (Takekawa et al., 2003). Carbon mass is an essential factor during the transformation among different organics. Following Ervens et al. (2008), the total carbon chemical loss rate ( $\text{TC}_{\text{loss}}$ ) is defined as:

$$\text{TC}_{\text{loss}}(\text{kg C m}^{-3} \text{s}^{-1}) = 0.012 \times (5 \times L_{\text{isop}} + 7 \times L_{\text{tol}} + 10 \times L_{\text{pine}}) \quad (1)$$

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where  $L_{\text{isop}}$ ,  $L_{\text{pine}}$ , and  $L_{\text{tol}}$  are the loss rates (unit:  $\text{mol m}^{-3} \text{s}^{-1}$ ) of isoprene,  $\alpha$ -pinene, and toluene, respectively.

The concentrations of OH and  $\text{O}_3$  (unit:  $\text{m}^3 \cdot \text{m}^{-3}$ ) reflect the oxidation power of the atmosphere and can affect the reaction rate and pathway of SOA formation (Lim and Ziemann, 2005). VOC/ $\text{NO}_x$  could also be a significant factor to influence  $\text{SOA}_{\text{cl}}$  yields (Ervens et al., 2008). Information on cloud fraction has been partially enclosed in LWC since grid-box averaged LWC is used. Other factors related to cloud properties are not evaluated in this study.

The dependence of  $P_{\text{SOAcl}}$  on a variety of individual meteorological and chemical factors and their combinations are examined based on linear correlation analysis and multiple regression models. The best-fit equation is used to predict the global  $\text{SOA}_{\text{cl}}$  production.

### 3 Factors controlling $\text{SOA}_{\text{cl}}$ production

Associations between daily  $P_{\text{SOAcl}}$  and each of the six important factors (i.e. LWC,  $\text{TC}_{\text{loss}}$ , concentrations of OH and  $\text{O}_3$ , VOC/ $\text{NO}_x$ , and temperature) across all grid boxes below 200 hPa are examined by a correlation analysis with a sample size of approximately 95 million. The results are shown in Table 1 and is restricted to the following conditions: pressure level below 200 hPa, cloud volume fraction  $> 10^{-3}$ , LWC  $> 10^{-12} \text{ kg(water) kg(air)}^{-1}$ , and  $\text{TC}_{\text{loss}} > 10^{-22} \text{ kgC m}^{-3} \text{ s}^{-1}$ .

#### 3.1 Liquid water content

As shown in Table 1, LWC has the highest positive correlation ( $r = 0.32$ ) with  $P_{\text{SOAcl}}$  among the six factors, indicating that LWC is the most important factor determining  $P_{\text{SOAcl}}$  and more LWC enhances  $P_{\text{SOAcl}}$ . Figure 2a depicts the spatial distribution of the  $r$  values between  $P_{\text{SOAcl}}$  and LWC. High positive correlation ( $r > 0.7$ ) is found over a broad area around the world at both lower and higher altitudes (see Fig. S1a in

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the Supplement). Over the forest regions in South Africa and South America,  $P_{\text{SOA}_{\text{clid}}}$  has a particularly high correlation with LWC ( $r > 0.9$ ). This is because that when SOA precursors are abundant, LWC becomes the limiting factor determining the change of  $P_{\text{SOA}_{\text{clid}}}$ . Similarly, the high correlation over the Sahara regions may be also due to the lack of cloud water.  $\text{SOA}_{\text{clid}}$  will form immediately in these areas whenever cloud is present, even though the amount of precursors is trivial compared to other places.

### 3.2 Total carbon loss rate

$\text{TC}_{\text{loss}}$  represents the abundance of precursors and oxidation power, and thus reflects the production rate of water-soluble organic carbons (WSOC) in the gas phase. It ranks the second in terms of the correlation with  $\text{SOA}_{\text{clid}}$  production ( $r = 0.26$ , see Table 1). Figure 2b shows the horizontal distribution of the  $r$  values which are usually less than 0.7 except over Southeast China around 500 hPa (see Fig. S1b), Tibetan Plateau around 900 hPa, and a few locations over remote oceans, where  $\text{TC}_{\text{loss}}$  is strongly correlated with the  $P_{\text{SOA}_{\text{clid}}}$  ( $r > 0.7$ ). This indicates that  $\text{TC}_{\text{loss}}$  acts more effectively there to facilitate  $\text{SOA}_{\text{clid}}$  formation.

### 3.3 Temperature

As indicated in Table 1 temperature plays a minor role in  $P_{\text{SOA}_{\text{clid}}}$ . The  $r$  value between  $P_{\text{SOA}_{\text{clid}}}$  and temperature is typically small ( $< 0.3$ ) around the world (Fig. 2c). This suggests that the effects of temperature on  $\text{SOA}_{\text{clid}}$  formation are either irrelevant or nonlinear. However, relatively high correlation ( $r > 0.5$ ) is found over Northeast Asia, where  $\text{TC}_{\text{loss}}$  also plays an important role. This indicates that temperature maybe indirectly affects  $P_{\text{SOA}_{\text{clid}}}$  by influencing  $\text{TC}_{\text{loss}}$  or chemistry in this region. It is also possible that cloud formation and LWC is dependent on temperature in certain places like Northeast Asia.

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### 3.4 Other factors

Similar to temperature, the effects of oxidants (i.e. OH and O<sub>3</sub>) on  $P_{\text{SOA}_{\text{cld}}}$  are embedded in both gas-phase and aqueous-phase chemistry. Since  $\text{TC}_{\text{loss}}$  alone may only represent the gas-phase oxidation power, we evaluate the overall effect of O<sub>3</sub> and OH on  $\text{SOA}_{\text{cld}}$  in Fig. 2d, e, respectively. Both the cross-regional correlation (Table 1) and the spatial distribution of  $r$  show little association between  $P_{\text{SOA}_{\text{cld}}}$  and these two oxidants, indicating that oxidant alone is not linearly determining the overall gaseous and aqueous processes of  $\text{SOA}_{\text{cld}}$  formation or that oxidant is never limiting during the in-cloud process.

VOC/NO<sub>x</sub> is also a good predictor of  $\text{SOA}_{\text{cld}}$  production (Ervens et al., 2008). However, the cross-regional correlation between VOC/NO<sub>x</sub> and  $P_{\text{SOA}_{\text{cld}}}$  shows little association (Table 1). By examining the correlations over different locations, we find weak negative correlations distribute over most places (Fig. 2f), consistent to the findings in Ervens et al. (2008) that  $\text{SOA}_{\text{cld}}$  production increases as VOC/NO<sub>x</sub> decreases.

Correlations between the logarithm of  $P_{\text{SOA}_{\text{cld}}}$  ( $\log(P_{\text{SOA}_{\text{cld}}})$ ) and the logarithm of the six factors are also shown in Table 1. High correlations are found for all factors except VOC/NO<sub>x</sub>, indicating significant nonlinear association between  $P_{\text{SOA}_{\text{cld}}}$  and each factors. Table 2 shows the results of a multiple linear regression between  $\log(P_{\text{SOA}_{\text{cld}}})$  and the logarithm of these factors. From the standardized regression coefficients (i.e. the  $B$  values), LWC and  $\text{TC}_{\text{loss}}$  are still the two dominant factors contributing to  $P_{\text{SOA}_{\text{cld}}}$ .

### 4 Parameterization of $\text{SOA}_{\text{cld}}$ production

Above analysis indicates that among the six factors, LWC and  $\text{TC}_{\text{loss}}$  are the two most significant factors affecting in-cloud production of SOA. Results of the multiple linear regression model in Table 2 indicate that  $P_{\text{SOA}_{\text{cld}}}$  is driven by both LWC and  $\text{TC}_{\text{loss}}$ , with the best-fit relationship shown in Eq. (2):

$$P_{\text{SOA}_{\text{cld}}} = \alpha \times \text{LWC} \times \text{TC}_{\text{loss}}^{\gamma} + \beta \quad (2)$$

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where  $\alpha$ ,  $\beta$ , and  $\gamma$  are constants. The best estimated global uniform values for  $\alpha$ ,  $\beta$ , and  $\gamma$  in Eq. (2) are  $4.66 \times 10^{-5}$ ,  $0.84 \times 10^{-17}$ , and 0.4, respectively. The cross regional  $R^2$  of Eq. (2) is approximately 0.5, indicating that the combination of LWC and  $TC_{\text{loss}}$  alone can explain nearly half of the spatial and temporal variability of  $P_{\text{SOA}_{\text{cld}}}$  in a global scale. Equation (2) can be applied globally with the following restrictions (i.e. cloud volume fraction  $> 10^{-3}$ ,  $LWC > 10^{-12} \text{kg}(\text{water}) \text{kg}(\text{air})^{-1}$ ,  $TC_{\text{loss}} > 10^{-22} \text{kgCm}^{-3} \text{s}^{-1}$ , and pressure level below 200 hPa).

Equation (2) also indicates that the production of  $\text{SOA}_{\text{cld}}$  is simultaneously determined by LWC and  $TC_{\text{loss}}$ , which, respectively, represent the contribution from liquid-phase processes and gas-phase processes. The parameter  $\alpha$  denotes the annual average intensity of chemical reactions in these processes, and the parameter  $\beta$  probably represents the annual average influence of some physical processes, such as the transport of  $\text{SOA}_{\text{cld}}$  precursors from other regions. Besides  $\alpha$  and  $\beta$ , we find exponents of LWC and  $TC_{\text{loss}}$  are approximately 1 and 0.4, respectively. This indicates that  $P_{\text{SOA}_{\text{cld}}}$  responses linearly to the variability of cloud liquid water, but nonlinearly (or concavely) to the gas-phase oxidation of hydrocarbons. The  $\gamma$  value reflects the complexity and combined effects of multiphase processes from the oxidation of VOCs to  $\text{SOA}_{\text{cld}}$  formation, including production of water-soluble species in the gas phase, the gas-liquid transport of oxidation products, and subsequent chemical reactions inside cloud droplets. It may also suggest that only a portion of the species generated from isoprene (or other VOCs) oxidation are involved in the cloud processes to produce SOA.

## 5 Model evaluation

The global  $\text{SOA}_{\text{cld}}$  production is estimated to be  $22.3 \text{Tgyr}^{-1}$  by Eq. (2), slightly lower ( $-5\%$ ) than the estimation based on detailed cloud chemistry. Specifically, the total  $\text{SOA}_{\text{cld}}$  production tends to be underestimated in JJA ( $-18\%$ ) and SON ( $-10\%$ ), but overestimated in MAM ( $5.5\%$ ) and DJF ( $9.5\%$ ).

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Figure 3 compares the parameterized and process-based annual mean  $P_{\text{SOA}_{\text{clid}}}$  for all grid boxes around the world. The parameterized  $P_{\text{SOA}_{\text{clid}}}$  is in general within a factor of 4 (representing 94 % of global  $\text{SOA}_{\text{clid}}$  mass production) but mostly within a factor of 2 (accounting for 70 % of global  $\text{SOA}_{\text{clid}}$  mass production) of these process-based estimations. The yellow dots in Fig. 3 represent grids at high altitudes (above 400 hPa) as well as two polar regions (90° S–66.5° S, 66.5° N–90° N) below 400 hPa, whereas the blue part mostly represents tropical and mid-latitude regions below 400 hPa, where 95 % of global  $\text{SOA}_{\text{clid}}$  mass is produced. Even though the yellow dots represent 40 % of the world grid cells, they only account for  $\sim 5$  % of total global  $\text{SOA}_{\text{clid}}$  mass production.

Figure 4 further decomposes the yellow dots in Fig. 3 into three parts: high-altitude regions (above 400 hPa), Antarctic regions (90° S–66.5° S, below 400 hPa), and Arctic regions (66.5° N–90° N, below 400 hPa). We find that  $P_{\text{SOA}_{\text{clid}}}$  over the Arctic are predicted well by Eq. (2), and nearly 70 % of grid cells are within a factor of 2 of the process-based estimations. In contrast, the  $P_{\text{SOA}_{\text{clid}}}$  over the Antarctic and high-altitude regions are being significantly overestimated (more than 85 % of these places are overestimated by more than a factor of 4). However, the  $\text{SOA}_{\text{clid}}$  mass production over these two regions are negligibly small ( $< 3$  % of the total global  $\text{SOA}_{\text{clid}}$  mass production).

The process-based and parameterized annual column and zonal mean production of  $\text{SOA}_{\text{clid}}$  are shown in Figs. 5 and 6, respectively. Both horizontal and vertical distributions of parameterized results are consistent well with the process-based estimations, except that more than a factor of 2 underestimation is observed over the southeastern coast of South America and Northeastern China, and a factor of 2–5 overestimations near the equatorial regions above 350 hPa. In addition, the distribution of parameterized  $P_{\text{SOA}_{\text{clid}}}$  follows a similar seasonal variation pattern with the process-based results (Figs. S2 and S3 in the Supplement). The  $\text{SOA}_{\text{clid}}$  production over the southeastern coast of South America is systematically underestimated throughout the year, probably due to the spatial variability of  $\text{SOA}_{\text{clid}}$  production efficiency (represented by the parameter  $\alpha$  in Eq. 2) which might be larger in this area than the global averaged value. In JJA,  $P_{\text{SOA}_{\text{clid}}}$  is also underestimated significantly over the boreal forests in Eastern Rus-

sia and Canada. The reason lies in that factors, such as temperature,  $O_3$ , VOC/ $NO_x$ , etc, may also facilitate  $P_{SOA_{cl d}}$  but are not incorporated in Eq. (2). The vertical profiles of the parameterized  $P_{SOA_{cl d}}$  are in general consistent well with the process-based results (Figs. S4 and S5 in the Supplement), except that  $P_{SOA_{cl d}}$  is relatively overestimated above 400 hPa, where the absolute mass production is trivial.

## 6 Sensitivity and uncertainty analysis

### 6.1 Sensitivity test

In order to understand how sensitive that  $P_{SOA_{cl d}}$  depends on parameters (i.e.  $\alpha$ ,  $\beta$ , and  $\gamma$ ) used in Eq. (2), we conduct six sensitivity tests by either increasing or decreasing each parameter by 20%. As shown in Table 3, the global production of  $SOA_{cl d}$  is determined linearly by  $\alpha$ , but is less influenced by  $\beta$  (e.g. a 20% change in parameter  $\beta$  only results in  $\sim 0.5\%$  change in global  $SOA_{cl d}$  production). Global  $P_{SOA_{cl d}}$  is also sensitive to  $\gamma$ , but exhibits a nonlinear relationship.

Figure 7 shows the relative change in column and zonal mean production of  $SOA_{cl d}$  when parameter  $\alpha$ ,  $\beta$  and  $\gamma$  are increased by 20% (the results show similar pattern if these parameters are decreased by 20%). As shown in Fig. 7a, b,  $P_{SOA_{cl d}}$  is very sensitive to  $\alpha$  all over the world except the Antarctic and high-altitude regions, where parameter  $\beta$  has a dominant effect (Fig. 7c, d). Figure 7e, f (and Fig. S6 and S7 in the Supplement) show the change in  $P_{SOA_{cl d}}$  when parameter  $\gamma$  is increased by 20%. As inferred by Eq. (2),  $\gamma$  is the only parameter leading to the nonlinear change in  $P_{SOA_{cl d}}$ , mainly driven by the seasonal change in  $TC_{loss}$ . During boreal winters (DJF) when  $TC_{loss}$  is small,  $P_{SOA_{cl d}}$  is insensitive to  $\gamma$  over almost all continents in the Northern Hemisphere. Conversely, during boreal summers (JJA), the  $P_{SOA_{cl d}}$  in these continents is changed by 20%–40% with a 20% change in  $\gamma$ , particularly at lower altitudes. Over the tropical forests, (i.e. South Africa and the Amazon regions),  $P_{SOA_{cl d}}$  is sensitive to  $\gamma$  for all seasons.

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## 6.2 Uncertainties

Uncertainties of the parameterized  $\text{SOA}_{\text{cld}}$  production could be embedded in the following three aspects: (1) the variance that is not explained by the linear regression model; (2) effects of cloud lifetime, cloud droplet size and cloud entrainment rate on  $P_{\text{SOA}_{\text{cld}}}$  (which will be evaluated in the follow-up studies); (3) biases passing from the process-based model (i.e. simulations of cloud, transport and gas and liquid phase chemistry).

The  $\text{SOA}_{\text{cld}}$  formation includes a series of complicated physical and chemical processes and is influenced by many factors involving meteorological conditions, precursor emissions, atmospheric transport, photochemical and aqueous reactions. As mentioned in Sect. 5, biases still exist in the parameterized results. This mainly due to that our parameterization on the production of  $\text{SOA}_{\text{cld}}$  (i.e. Eq. 2) only focus on the two most important factors. For example, the underestimation of  $P_{\text{SOA}_{\text{cld}}}$  in Northeast Asia may be caused by neglecting the contribution from temperature, which has shown to be correlated with  $P_{\text{SOA}_{\text{cld}}}$  over this region ( $r > 0.5$ ). In addition, the three parameters in Eq. (2) just represent part of the detailed chemical and physical information and may not be able to fully capture all the processes of multiple phase chemistry for cloud SOA formation, such as partitioning, oxidation, and so on.

To reduce the bias of  $\text{SOA}_{\text{cld}}$  parameterization, one possible way is to improve the parameter  $\alpha$  and  $\gamma$  in Eq. (2). These two parameters directly control the overall magnitude of  $\text{SOA}_{\text{cld}}$  production, and are dependent on seasons. Therefore, further decomposing  $\alpha$  and  $\gamma$  by season could reduce the underestimation in JJA and SON and the overestimation in DJF and MAM. In addition, rather than relying on one set of global uniform parameters, Eq. (2) can be improved by a variety of sets of parameters conditioning on either VOCs/ $\text{NO}_x$  ratios or different locations (i.e. polar region, continents, remote oceanic regions, etc.). Furthermore, besides LWC and  $\text{TC}_{\text{loss}}$ , more factors (e.g. temperature and VOC/ $\text{NO}_x$ ) could be used to improve the parameterization over

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a specific region (e.g. the Northeastern Asia). Such detailed regional analysis is beyond the scope of this study, and will be investigated in our follow-up studies.

## 7 Conclusions

As a critical component of the atmospheric particulate matter burden,  $SOA_{\text{cld}}$  plays a crucial role in the atmospheric chemistry. Recently, in-cloud process has been shown to contribute to atmospheric organic aerosol mass. Based on a detailed cloud chemistry scheme, Liu et al. (2012) has found that substantial  $SOA_{\text{cld}}$  are formed in the tropical and mid-latitude regions of the lower troposphere. This could potentially fill the gap between the observed and modeled organic aerosols at higher altitudes, as found in Carlton et al. (2008). Our study is based on the framework developed in Liu et al. (2012), but focuses mainly on firstly identifying the principal factors that govern the overall cloud processes generating SOA, and secondly exploring a relationship of the relevant factors which can efficiently represent the global  $SOA_{\text{cld}}$  production with reasonable temporal and spatial variability.

We conduct a simulation of in-cloud production of SOA based on the GFDL coupled chemistry-climate model AM3 with detailed gaseous and aqueous phase chemistry. The correlation between  $SOA_{\text{cld}}$  production and each of six potential factors (i.e. LWC,  $TC_{\text{loss}}$ , temperature,  $VOC/NO_x$ , OH, and  $O_3$ ) is examined. We find that LWC determines the spatial pattern of  $SOA_{\text{cld}}$  formation, particularly over tropical, subtropical and temperate forest regions.  $TC_{\text{loss}}$  ranks the second and mostly represent the seasonal variability of vegetation growth and the rate of gas-phase chemical reactions. Other individual factors show little linear correlation to  $SOA_{\text{cld}}$  production. We find that the rate of  $SOA_{\text{cld}}$  production is simultaneously determined by both LWC and  $TC_{\text{loss}}$ , but responds linearly to LWC and nonlinearly to  $TC_{\text{loss}}$  (i.e.  $TC_{\text{loss}}^{0.4}$ ). This parameterization can capture well the spatial and temporal variability of global process-based  $SOA_{\text{cld}}$  formation, especially in regions below 400 hPa and places excluding remote oceans and the Antarctic region.

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In order to identify the corresponding change of SOA<sub>cl</sub> production resulting from the perturbations of each parameter (i.e.  $\alpha$ ,  $\beta$  and  $\gamma$  in Eq. 2), we conduct six sensitivity tests in which each parameter is either increased or decreased by 20 % while keeping the other two parameters unchanged. We find that the SOA<sub>cl</sub> production is sensitive to parameters  $\alpha$  and  $\gamma$  in most areas around the world. But the parameter  $\beta$  has dominant contributions to the SOA<sub>cl</sub> production over the Antarctic and high-altitude regions where LWC and TC<sub>loss</sub> are very small.

This parameterized in-cloud SOA production can be easily applied to either global chemical transport models or global coupled chemistry-climate models to efficiently and reasonably simulate the SOA production from cloud processes.

**Supplementary material related to this article is available online at:**

**<http://www.atmos-chem-phys-discuss.net/12/26929/2012/acpd-12-26929-2012-supplement.pdf>**

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**Table 1.** Correlation between daily SOA<sub>cloud</sub> production rate ( $P_{\text{SOA}_{\text{cloud}}}$ ) and each individual factor.

Correlation <sup>1</sup>	LWC	TC <sub>loss</sub>	Temperature	O <sub>3</sub>	OH	VOC/NO <sub>x</sub>
$r$	0.32	0.26	0.036	-0.001	-0.008	-0.006
$r_{\log}^2$	0.96	0.97	-0.98	0.97	0.95	0.074

<sup>1</sup> All p values are less than 0.001.

<sup>2</sup> The correlation coefficients ( $r$ ) between  $\log(P_{\text{SOA}_{\text{cloud}}})$  and the logarithm of each individual factor.

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**Table 2.** Multiple linear regression between  $\log(P_{\text{SOAcid}})$  and the logarithm of six factors.

	LWC	TC <sub>loss</sub>	Temperature	O <sub>3</sub>	OH	VOC/NO <sub>x</sub>
$b^1$	1.0409 ± 0.0002	0.3416 ± 0.0003	14.77 ± 0.01	-0.207 ± 0.002	-0.0106 ± 0.0005	0.0397 ± 0.0004
$B^2$	0.1704	0.0957	0.0571	-0.0052	-0.0015	0.0085
$b^3$	1.0515 ± 0.0002	0.4175 ± 0.0002				
$B^3$	0.1721	0.1170				

<sup>1</sup>  $b$  is the partial regression coefficients of each individual factor with 95 % confidence intervals (the regression result:  $R^2 > 0.95$ ).

<sup>2</sup>  $B$  represents the standardized regression coefficients (i.e. the partial regression coefficients in units of standard deviation), which can be used to compare and explore the most effective factors.

<sup>3</sup> Results based only on the most effective factors (i.e. LWC and TC<sub>loss</sub>).

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**Table 3.** The relative change in  $SOA_{\text{cld}}$  production as a 20% change of each parameter in Eq. (2).

Parameter	Relative change(%)	Relative change (%) in $SOA_{\text{cld}}$ production				
		DJF	MAM	JJA	SON	Annually
$\alpha$	20	19.45	19.42	19.51	19.43	19.46
	-20	-19.45	-19.42	-19.51	-19.43	-19.46
$\beta$	20	0.55	0.58	0.49	0.57	0.54
	-20	-0.55	-0.58	-0.49	-0.57	-0.54
$\gamma$	20	17.65	17.05	17.86	14.73	16.87
	-20	-9.95	-9.52	-10.29	-7.95	-9.46

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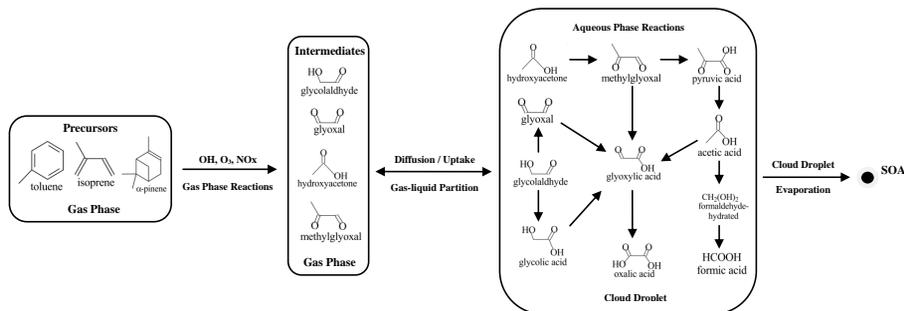


Fig. 1. Chemical mechanism for aqueous-phase formation of SOA.

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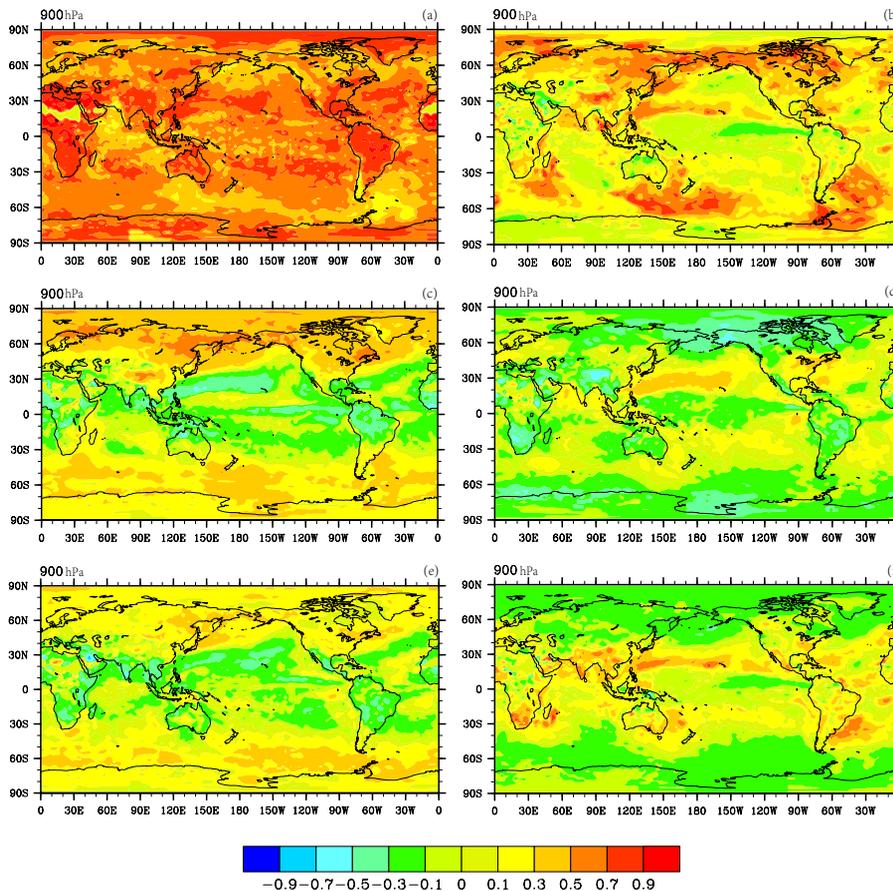
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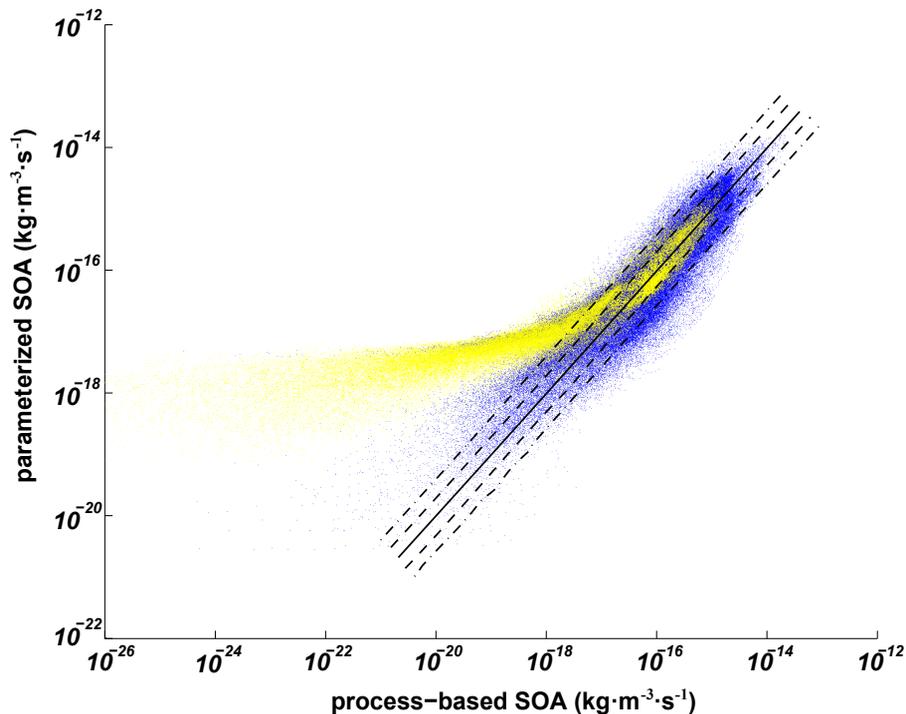
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**Fig. 2.** Distribution of the correlation ( $r$ ) between SOA<sub>cl</sub> production and (a) LWC, (b) TC<sub>loss</sub>, (c) temperature, (d) O<sub>3</sub>, (e) OH, (f) VOC/NO<sub>x</sub> at 900 hPa round the world.



**Fig. 3.** Comparison between the parameterized and process-based annual mean  $P_{\text{SOAcl d}}$  for every grid box below 200 hPa. Yellow dots indicate two polar regions as well as altitudes above 400 hPa. The solid line indicates the 1 : 1 line; the dashed lines indicate the 1 : 2 (or 2 : 1) lines; the dash-dot lines indicate the 1 : 4 (or 4 : 1) lines.

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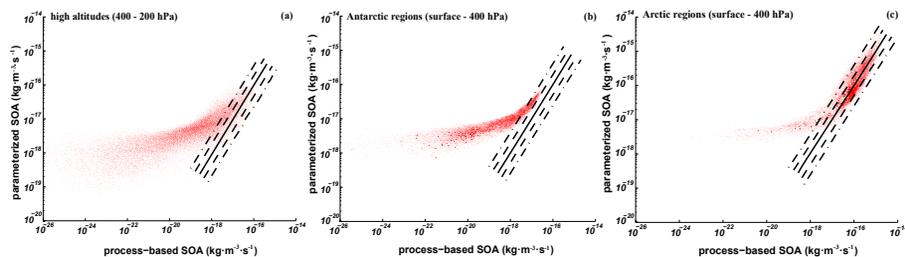
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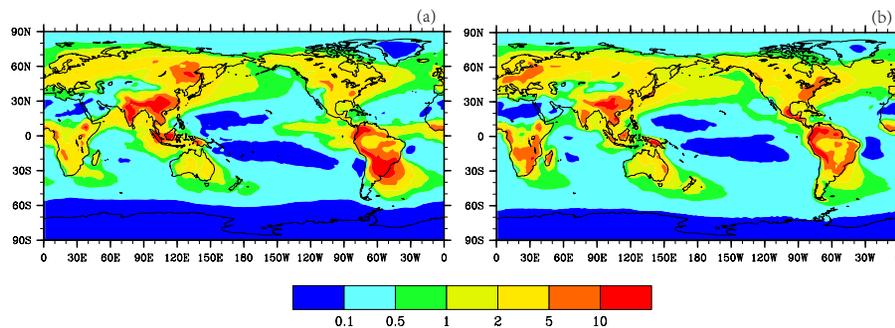


**Fig. 4.** Same as Fig. 3, but only for **(a)** high altitudes (above 400 hPa), **(b)** Antarctic regions, and **(c)** Arctic regions.

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**Fig. 5.** Process-based (a) and parameterized (b) annual averaged column production of SOA<sub>cl</sub> (unit:  $\text{ngm}^{-2} \text{s}^{-1}$ )

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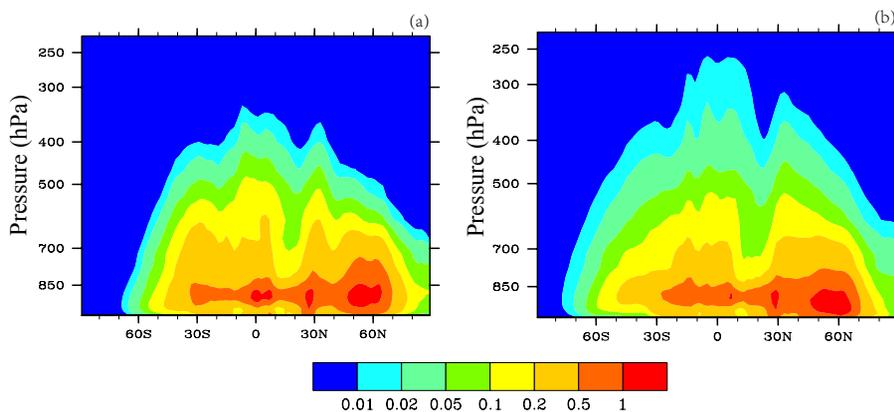
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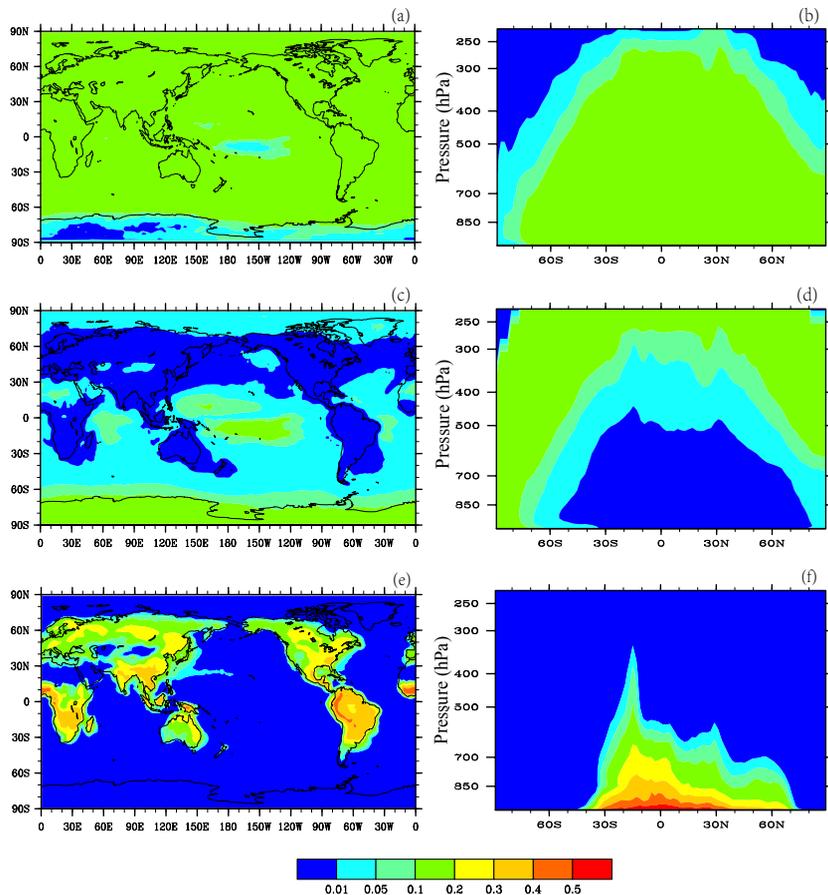
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**Fig. 6.** Process-based **(a)** and Parameterized **(b)** annual averaged zonal mean production of  $\text{SOA}_{\text{cl,d}}$  (unit:  $\text{pg m}^{-3} \text{s}^{-1}$ ).

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**Fig. 7.** Relative change of annual averaged column (a, c, e) and zonal mean (b, d, f) production of SOA<sub>old</sub> as a result of 20% increase in parameter  $\alpha$  (a, b),  $\beta$  (c, d), and  $\gamma$  (e, f).